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THE RELATION OF OSMOTIC PRESSURE TO TEMPERATURE.[1]

PART I. THE MANUFACTURE OF THE CELLS EMPLOYED IN THE MEASUREMENTS.

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In our last paper[2] upon the osmotic pressure of cane sugar solutions, an account was given of the then recent work at 20°, and a comparison was made of the results at this temperature with those which had previously been obtained at 0°, 5°, 10°, 15° and 25°. The experimental evidence which was then brought together, covering, at intervals of five degrees, the whole range of temperature from 0° to 25°, pointed unmistakably to the probable existence—for any given concentration of solution—of a constant ratio of osmotic to gas pressure; to the conclusion, in other words, that within these limits of temperature the temperature coefficient of osmotic pressure is, in the case of cane sugar, identical with that of gases.

The evidence was not of equal value throughout; for, during the progress of the work, the method had been steadily

[1] The work upon osmotic pressure which has been in progress in this laboratory during the past 10 years is aided by grants from the Carnegie Institution. The earlier papers upon the subject will be found in THIS JOURNAL, **26**, 80; **28**, 1; **29**, 173; **32**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425 and 558; **38**, 175; **39**, 667; **40**, 1, 194, 266 and 325; **41**, 1, 92 and 257.

[2] THIS JOURNAL, **41**, 256.

improved, and one after another of the principal sources of error had been eliminated or reduced, so that each series of measurements was made under more satisfactory conditions than the one which preceded it. The progress in these respects had been so considerable that the results which were obtained at the lower temperatures might well be considered as crude and as much less trustworthy than those at the higher temperatures. Nevertheless, the results, even at 0°, 5° and 10°, were in fair quantitative accord as to the equality of the temperature coefficients of osmotic and gas pressures. Those at the higher temperatures, namely 15°, 20° and 25°, were strikingly so.

We did not consider the evidence which was offered sufficient to *prove* the equality of the coefficients in question, but rather as establishing a strong probability of it. Our attitude in the matter was expressed in the following words: "We do not permit ourselves, as yet, to entertain any *views* regarding the proper magnitude of osmotic pressure at any temperature; nevertheless we are prepared to state that all the best experimental evidence which we are now securing is tending strongly in the direction of establishing the substantial equivalence of the temperature coefficients of osmotic and gas pressure." The statement was intended, of course, to apply only within the field over which we had worked with care, namely, to cane sugar solutions ranging in concentration from 0.1 to 1.0 weight normal, and to temperatures between 0° and 25°.

In planning for the continuance of the work, it seemed best to devote our efforts principally to the further investigation of the relation of osmotic pressure to temperature, and to repeat, for that purpose, with all possible care, the work already done, rather than to bring other substances into the investigation or to experiment at temperatures above 25°. On the experimental side of osmotic pressure, the main problems for the present are: (1) what is its relation to temperature? and (2) what is its relation to concentration? To some extent, the investigation of both questions is necessarily simultaneous; but under present conditions the second may

be kept somewhat in the background to the advantage of the first, for the reason that it is *easier* to determine, with a satisfactory degree of precision, the relation of pressure to temperature than its relation to concentration. We shall have occasion, at a later period, to discuss this matter in detail, but for the present it will suffice to recall, by way of explanation, the fact that in determining the temperature coefficient the unknown and indeterminable errors of the manometers are of much less importance than in determining the relation of pressure to concentration; since, in the former case, the pressures to be compared, *i. e.*, those of a given concentration at different temperatures, being approximately equal, errors of meniscus, of variable capillary depression, *etc.*, affect all the measurements in about an equal degree; whereas, in the second case, the pressures to be compared differ widely, and since the nitrogen gas occupies very different proportions of the manometer at different times, the local errors of the instrument affect the results unequally.

We have already nearly finished a repetition of the work at the six different temperatures mentioned above, and it is our purpose to describe, in this paper and in those which will follow it, the conditions under which it was carried out. A somewhat detailed account of the investigation will be given in order to enable others to judge justly what weight is to be attached to the results. As for ourselves, we are prepared to say that they appear *sufficiently to establish the equality of the temperature coefficients of osmotic and gas pressures.* We wish to emphasize again, however, the fact that the conclusion applies for the present only to cane sugar solutions between 0° and 25° and to concentrations of that substance which range from one-tenth to one gram-molecular weight dissolved in 1,000 grams of water. The ratio of osmotic to gas pressure has been found to remain (for any given concentration) very nearly constant up to 25°. What will be found at higher temperatures cannot yet be affirmed with certainty, but a few apparently reliable preliminary measurements, made on concentrated solutions at 30°, 40° and 50°, indicate that the ratio will be found to diminish at the higher tempera-

tures, the decline beginning at some point between 25° and 30°. Any discussion at the present time of the cause of this apparent *dilution* of cane sugar solutions at temperatures above 25°—*i. e.*, whether it is due to a breaking down of the complexes of water molecules, to the dissociation of hydrates, or to some other change in molecular relations—would be premature owing to the meagerness of the established and pertinent facts in the case; and we mention it only because the hope seems to be already justified that the study of osmotic pressure at the higher temperatures, which will soon be undertaken, will throw much needed light upon the states of the solvent at different temperatures.

Before passing on to matters of method and procedure in the investigations of the past two years, we may be permitted to refer to certain facts which have doubtless contributed materially to the thoroughness of the work, and, we hope, to the trustworthiness of the results. It was realized quite early that the task we had undertaken was beset on all sides by great and unusual experimental difficulties; and that to so far master these that the results should be really convincing, more than the working lifetime of any one individual must be devoted to the undertaking. That we did not overestimate the magnitude of the difficulties to be encountered is shown by the fact that it has taken ten years of time, and—counted as the work of one man—over forty-five years of labor, merely to develop the method and to demonstrate to our satisfaction that the osmotic pressure of one substance obeys, within certain narrow limits of temperature, the law of Gay-Lussac for gases.

It also became apparent very early in the course of the investigation that this work—in which the success of an experiment depends upon the perfection of every one of a multitude of conditions, and in which failure is sure to follow the slightest neglect of any one of a great number of details—offers very unusual opportunities for self-deception as to the trustworthiness of the results.

The conviction that a condition of wariness and of distrustful caution on the part of the experimenter is indispensa-

ble has grown with our experience, until—after having made more than 3,000 quantitative experiments with osmotic cells—we are ready to affirm that no result as to the magnitude of osmotic pressure should be accepted until it has been confirmed by every practicable test, and, moreover, that every result which depends in any degree upon the *estimated* effects of hypothetical or unmeasured conditions should be unceremoniously rejected. By way of justifying this attitude, we will state, on the basis of our own experience, that, with imperfect methods and insufficient control of results, almost any view regarding the magnitude of osmotic pressure can be made exceedingly plausible.

In view of the magnitude of the difficulties to be overcome and especially the dangers of misinterpretation of results, it seemed to us that the value of the outcome would depend very largely upon our freedom from any preconceived notions as to what the results *ought* to be. Accordingly, we have endeavored to carry out the work without any personal convictions or beliefs in regard to the true osmotic pressure of solutions under any conditions of temperature or concentration, that is, without anything in mind which was to be *proved* or *disproved*.

The reasons for regarding the evidence brought together in our last paper as insufficient to establish beyond question the temperature coefficient of the osmotic pressure of cane sugar solutions between 0° and 25° may be summarized as follows:

1. The earlier series of measurements had been carried out with imperfect facilities for the automatic regulation of temperature, and fluctuations of bath temperature had occurred which we afterwards came to consider quite intolerable. The subject of "*thermometer effects*" in the cell, *i. e.*, the expansion and contraction of the cell contents, has frequently been mentioned in former papers as one of the serious difficulties in the way of the correct measurement of osmotic pressure, but we did not fully realize how great effects may be produced by even small fluctuations of temperature until we had succeeded by means of improvements in the cells

and the membranes in suppressing all dilution of the cell contents. After this had been accomplished, the observed fluctuations in pressure—after a maximum had been reached—could only be ascribed to irregularities of bath temperature, and to variations in atmospheric pressure. The effect of the latter, however, is relatively small except in the case of dilute solutions and its limits can be determined. In the course of the work at 20°, where there was no dilution of the cell contents which could be detected by the polariscope, it was found that a change of 0°.01 to 0°.02 in the bath temperature, unless distributed over a long period, was capable of producing distinct *thermometer effects*. This observation necessarily brought under suspicion the results in the earlier series, where the fluctuations in bath temperature had been much greater.

2. In all the six series of measurements, except that at 20°, there had been some occasional decrease in the concentration of the cell contents. In the first two series—those at 0° and 5°—a decrease had occurred in the majority of the experiments which amounted to an average of 1.73 and 1.45 per cent., respectively; while in the series at 10°, 15° and 25° it amounted to an average of 0.22, 0.10 and 0.20 per cent., respectively. Only the series at 20°, the last one, was faultless in respect to the dilution of the cell contents. As long as we were unable to suppress it altogether, we had endeavored to interpret this dilution or, rather, loss in rotation of the cell contents, and to estimate its effect upon the observed apparent osmotic pressure. But, unfortunately, the applicability of the corrections which were made depended on the correctness of our interpretation of the causes of the observed loss in rotation; and every explanation of this phenomenon which we have hitherto given has proved in the course of time to be either partly wrong or not wholly adequate. At first, we ascribed the loss in rotation mainly to an *inversion* of the cane sugar, but it subsequently appeared that the inversion which takes place in the closed cell is insignificant. One effect of correcting the loss in rotation as being due to inversion was to make it appear that the osmotic pressure of cane sugar solu-

tions is nearly proportional to concentration, whereas it afterwards became apparent that it runs nearly parallel with the freezing-point depressions. Later, the dilution of the cell contents was ascribed to certain conditions attending the closing and opening of the cells. But, since modifications of the cells which removed these conditions did not entirely suppress the dilution, it became certain that this explanation, though probably correct in the main, was not sufficient, and that the loss in rotation formerly observed was due, not to inversion, nor altogether to dilution at the time of closing and opening the cells, but to some extent to the imperfection of the membranes.

3. In the earlier work, the manometers had been filled with air. But it was found that in the instruments so filled the gas volume steadily diminished, and in time to an extent which had a sensible effect upon the apparent magnitude of the pressure. The changes in volume were ascertained from time to time, but probably not with the frequency which the importance of the matter demanded.

4. It is essential that the material used in determining a temperature coefficient shall be uniform in every particular. This is much more important, of course, than a high degree of purity. But the material which had been employed in the six series of measurements was not uniform throughout. The supply which had been used at 0°, 5°, 10°, 15° and 25° became exhausted while the work at 20° was in progress, and it was found that supposedly equivalent solutions of the old and the new materials did not give identical pressures.

Any one of the defects enumerated above would have afforded a sufficient justification for a repetition of the whole work; and, fortunately, we could undertake the task with a considerable degree of confidence in the value of the outcome, because the method of measuring osmotic pressure had already been developed and improved to a point where, in later work, we could nearly eliminate all of the faults which led us to distrust more or less the results of the earlier experiments. The cells and membranes had been so perfected that we were able to carry out the measurements of pressure without de-

crease in concentration in the cell contents. The facilities for the automatic regulation of temperatures had been improved until we could maintain, continuously for months, any desired temperature, with extreme variations not exceeding 0°.01 or 0°.02. Moreover, the manometers had all been recalibrated and refilled with nitrogen. As for the material for the solutions, which had failed at a critical time in the earlier investigation, we began with a supply of 75 kilograms of rock candy and purified it by repeated precipitations with alcohol, thus securing a supply of uniform material which was ample, not only for the work which is to be reported, but probably for any future experiments on the osmotic pressure of cane sugar solutions.

THE CELLS.

Much of the time during the past ten years has been spent in experimental work in the manufacture of cells. The first four years were devoted almost exclusively to that problem; and as the result of so much effort we had, at the end of this period, *two* cells with which we could measure osmotic pressure with some degree of confidence. At the present time we have about 30 cells which are suitable for the work. If these were lost, they could probably be replaced by an equal number of other cells in about two years' time. These statements will suffice to show that the problem of cell-making has been a very difficult one to solve. Certain qualities were found to be indispensable to the porous wall on which the membrane is deposited, and to secure all of these in one and the same product has cost much time and labor. Our earliest experience with porous cells was summarized in a paper published in 1905, as follows: "....it was supposed by the authors that, having solved in a satisfactory manner the problem of depositing the membranes, and having overcome, in a measure, the difficulties connected with the assembling of the different parts of the cell, they could proceed, without further delay, to the measurement of osmotic pressure. But it soon appeared that a third problem, the most difficult of all, remained to be dealt with, *i. e.*, the problem of the *porous*

wall. The porous cups in which the high pressures referred to had been obtained were a part of a lot of 100 which were made for the authors at a pottery in a neighboring city. Out of this number 25 or 30 had been found to answer the requirements[1] moderately well, and it was not doubted that others equally good, or better, could be readily procured. In this we were greatly mistaken, for among the nearly 500 cells which were subsequently made for us at various potteries, *not one* was found suitable for the measurement of osmotic pressure. The entire year was spent in procuring and testing porous cells from different sources, but to very little purpose except to convince us that the problem of producing the cells must be worked out in the laboratory rather than at the pottery." The quotation above includes about all that we have hitherto published on the subject of cell making.

The cells produced at the potteries were defective in various ways, but principally in the particulars enumerated below:

1. They were all lacking in the strength necessary to withstand any considerable outward pressure. Only one of the few which proved at all serviceable survived a pressure of 30 atmospheres, while most of them cracked under pressures below 20 atmospheres.

2. All of them contained numerous "*air blisters,*" which communicated with each other and with the interior surface of the porous wall in such ways as to give rise to the formation of a number of interior subsidiary membranes. Not infrequently, when the cell was broken for examination, as many as four or five of these minor membranes, often nearly parallel over a considerable area, were found in several localities; and it frequently happened also that the last of them was near, or even at, the exterior surface of the cell.

3. The cells obtained from the potters also lacked uniformity in respect to porosity. The same cell would often exhibit the greatest diversity in this respect. In some parts the structure would be as close as in porcelain, while in others it might be so open that the membrane was deposited nearly midway between the interior and exterior surfaces of the wall.

[1] As we then understood them.

A microscopic study of thin sections of the cells in which membranes had been deposited revealed the fact that—excluding the peculiar and often fantastic effects produced by "*air blisters*"—the location of the membrane is determined by the porosity of the cell wall. The more open the texture is, the more deeply within the wall will the deposition occur; while with a certain degree of closeness in this respect, the deposition is upon the *interior surface* of the cell.

After a somewhat protracted study of the cells which were first furnished by the potters, we thought ourselves able to formulate quite definitely the more important qualities which are essential to a satisfactory cell wall, and to state, in a general way, how some of these may be secured. It was clear:

1. That the materials used in making the cells must be *thoroughly mixed* in order to secure uniform porosity and uniform strength.

2. That, in order to secure *great strength*, the maximum allowable proportion of binding material (feldspar, *etc.*) must be employed—that proportion, in fact, which is just insufficient to convert the baking cell into porcelain.

3. That all *air blisters* must be eliminated.

4. That the texture of the cell wall must be so fine and uniform as to compel the deposition of the membrane exclusively upon the inner surface of the cell.

The reason for the suppression of air blisters and for the deposition of the membrane on the *interior* surface of the cell will appear if we consider the inequalities in the concentration of the solution which must result from its location elsewhere, *i. e.*, *within* the cell wall. In the latter case, owing to the slowness of diffusion in the wall, the liquid in the neighborhood of the membrane will be permanently less concentrated than the main body of the solution; while if the discharge of the entering water is from a free surface, the conditions will be favorable to the maintenance of uniform concentration throughout the enclosed solution.

Our observations and conclusions were duly communicated to the potters who were interesting themselves in our behalf, and they assured us of their confidence in their ability to pro-

duce cells with all of the required characteristics. But their expectations were not realized, as we have already stated; for, of the several hundred cells which were subsequently made for us, not one proved serviceable for the measurement of osmotic pressure. In fact, the later products were inferior to the earlier ones. In most of them, some of the faults which were to be avoided were greatly aggravated. This was notably the case in the matter of uniformity of porosity. The reasons for the failures of the potters afterwards became clear to us when, in attempting to manufacture for ourselves, we fell, from time to time, into some of the errors which had prevented their success.

Having become convinced that the correct texture of porous wall for the measurement of osmotic pressure cannot be produced by the usual methods of the potter, we proposed to them to resort to certain new practices. But coöperation along these lines was declined on the ground that, to one experienced in the ways of clays, our plans were obviously futile. Hence, as a last resort, the problem of cell making was taken from the pottery into the laboratory. The processes by which we were able ultimately to produce cells with faultless wall texture are, on the whole, simple, and they can be adequately described in few words; but their development cost us several years of pioneer experimental work.

The problem to which attention was first given was that of securing *uniform porosity* combined with *great and uniform strength*. To this end, the washed clays from several sources were mixed with varying quantities of ground feldspar, and the mixtures were burned at different temperatures, either in a calibrated electric furnace or in a Seger experimental kiln. The products were altogether disappointing. They were, in fact, quite as uneven in respect to porosity and strength as the cells which had been obtained from the potters. Thinking that our failure might be due, in part, to the coarseness of the materials, the clays and the feldspar were subjected to elutriation, and the wet mixtures of the finer portions thus obtained were then passed repeatedly through silk bolting cloth having 16,000 holes to the square

inch. The bolting process was followed by a long-continued churning of the mixture in water and, finally, by a most thorough kneading of the "putty." The results were still unsatisfactory, in that the porosity of the baked samples lacked the high degree of uniformity which is indispensable in the measurement of osmotic pressure. It was evident, moreover, on comparing our products with those of the potters, that we had been trying exactly what they had attempted except that they had omitted the elutriation and bolting processes to which we had resorted. We concluded that the necessary binding material *cannot* be successfully incorporated with the clays in the form of ground feldspar.

The final solution of the problem was easy and satisfactory. It occurred to us that perhaps sufficiently intimate admixtures might be obtained by bringing together two different clays, one of which is deficient in binding material while the other is overrich in that constituent. This was the plan which was adopted, and, with proper manipulation of the materials, it has never failed to give us products which, so far as we can discover, are perfect in respect to the uniformity of their porosity.

It remained to eradicate the air blisters which appear to be always present in cells made in the ordinary way, and to secure that degree of fineness of wall-texture which will cause the membrane to be deposited only upon the interior surface of the cell, and never sensibly within it. It is recalled here that, when the electrolytic deposition of the membrane is commenced, the cell wall which separates the two solutions is filled with water only, and that the position of the meeting place of the two kinds of ions is determined in great part by the size of the pores. If they are large, that is, if the wall-texture is what may be called an open one, the meeting place is within the wall, though always—in the absence of air blisters—somewhat nearer the interior than the exterior surface. If, on the other hand, the pores are small, the deposition occurs nearer the inner surface. Our problem was, of course, to produce a cell wall of such texture that the copper and ferrocyanide ions *must* meet just at the interior

ends of the pores, that is, we were to produce a cell wall in which the pores were, not only of a *uniform* diameter, but at the same time *excessively small*. This is necessary, not alone for the purpose already alluded to, namely, that of securing uniform concentration throughout the solution, but also to give to the membrane the *support from the rear* which will enable it to withstand high pressures. A membrane which is deposited in large pores is easily ruptured, and no membrane, obviously, is superior to its weakest part.

We had suggested to the potters two plans for removing the air blisters, and for securing at the same time that extremely dense texture of cell wall which was thought to be essential. The first of these was to form the cell itself under high pressure, while the second was to form the wet clay into a cylinder under great pressure, and from this to turn out the cell upon the lathe. Both plans were pronounced impracticable by the potters. After many months of futile effort, we were forced to agree with them as to the first project, but the alternative plan—that of pressing the clay into a cylinder and cutting the cell from this upon the lathe—was finally developed to a successful issue. We will pass over our attempts to form the finished cells under pressure as something more instructive to ourselves than helpful to others, and proceed to describe the present method of making cells which, when successful, gives an entirely satisfactory product.

A. Treatment of the Clays.

A considerable number of clays, both American and foreign, were investigated with reference to their suitability for the manufacture of cells, and two were finally selected as being, in our judgment, superior to all others for the purpose. These were a fire clay from Mt. Savage, Maryland,[1] and a so-called ball clay from Edgar, Florida.

The Flordia clay had been washed before it came into our hands, but both varieties were treated in the same manner for the purpose of separating the finer from the coarser materials. The process is as follows: Three empty alcohol

[1] The mine from which we obtained the fire clay has since become exhausted, and we are now searching for a substitute.

barrels, each with a spigot in the bung hole, are placed one above another, each of the upper two being set a little back of the one below it. The uppermost barrel is nearly filled with water, and into this is stirred about 3 kilograms of sifted clay. After standing quietly for three minutes, the spigot is opened and the contents of the upper half of the barrel are allowed to flow into the barrel below. The residue is removed and the barrel is recharged and again partially emptied, precisely as in the first instance. When the intermediate barrel is nearly full, its contents are likewise stirred and then allowed to settle for three minutes, after which the spigot is opened to allow the contents of the upper half of the barrel to run into the lowest receptacle. The material which collects in the last barrel is afterwards passed through silk bolting cloth having 16,000 holes to the square inch. The proportion of the original clay which is thus acquired for cell making is not very large. In one instance, where the weights of clay taken and of the final product were recorded, 500 pounds of the fire clay yielded 180 pounds of the product. In another case 200 pounds of the Edgar clay gave 75 pounds of the finer material.

It was found that the two clays, prepared as described above, mingle readily in all proportions, giving products which, when baked, are uniform in respect to texture and strength, and it was later ascertained that all the requirements of the situation are best met by mixing the two in about equal proportions by weight.

The process of mixing is as follows: (1) The two clays are mingled and repeatedly sifted in the dry state; (2) the mixture is then churned with water for several hours, after which (3) it is passed successively—without unnecessary interruption of the churning process—through two grades of bolting cloth, one of which has 16,000 and the other 26,000 holes to the square inch; (4) the material, after settling, is collected and drained upon a filter of bolting cloth resting upon one of paper; (5) it is then partially dried by heat; and, finally, (6) the mixture is kneaded upon a plate glass surface until, through evaporation of the excess of water, the "putty"

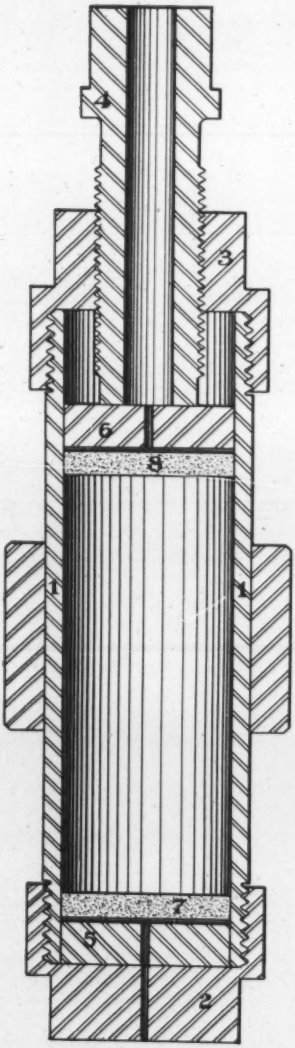


Fig. I.

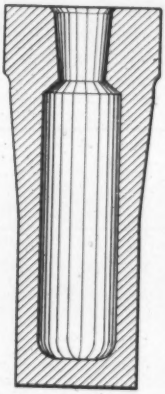


Fig. V.

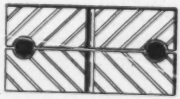


Fig. II.

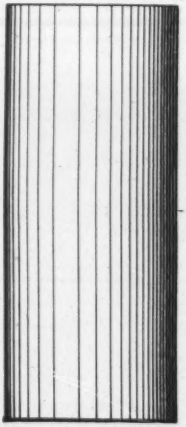


Fig. IV.

has attained the consistency which experience has shown to be best suited to pressing.

B. The Formation of the Cylinders.

A section of one of the steel presses in which the clay is compressed into cylinders is shown in Fig. I. The barrel (1) is threaded at both ends to receive the caps (2) and (3). The cap upon the lower end (2) is bored to permit the escape of the water which is squeezed out of the clay, while the cap upon the upper end (3) is bored and threaded internally to receive the hollow plug (4). The closely-fitting steel disks (5) and (6) are also bored to facilitate the escape of water. The disks (7) and (8) are of porous hard-burned clay, between which the clay is compressed by screwing down the plug (4) upon the steel disk (6). They may be replaced by disks of asbestos.

The upper steel disk (6) is less simple than it appears in the figure. In reality, two grooved disks, separated by hardened steel balls (bicycle balls), are used. The arrangement is shown in Fig. II. The upper half turns readily with the plug (4), which rests upon it, while the lower one remains stationary. If a single disk is employed, the clay is twisted in the direction of the screw thread, and the cell, when burned, exhibits upon its exterior surface a series of spirally arranged lines or depressions, as if the shrinkage of the clay in baking had not been entirely uniform.

Considerable difficulty was experienced at first in securing the correct temper for the steel disks, which should, of course, be equal to, but not much higher than that of the steel balls which separate them. If the disks are insufficiently tempered they are badly lacerated by the balls. On the other hand, if they are made too hard, they frequently crack under the great pressure to which the clay is subjected.

The device for compressing the clay is shown in Fig. III, without the framework which holds the various parts in their places. The press (1) containing the clay is secured between two flat bars of steel, a portion (2) of one of which is seen in the figure. The lower end of the shaft (3) is square in form

like the upper end of the plug (4) of Fig. I, and the collar (4), which joins the two, has a square hole of the same diameter passing through it. A portion of two of the timbers of the framework is shown at (5) and (6). Through these the shaft (3) slides freely up or down, except so far as its motion is limited by the set-collar (7). The large wooden drum (8) is firmly attached to the shaft and around it is wound the steel wire cable. The loose iron pulleys (9, 10, 11) serve to guide the cable. The large pulley (12) is situated in the attic of the laboratory. The cable, after leaving (11), ascends vertically through the ceiling of the room, and, after passing over the pulley (12), it returns and is terminated by the heavy iron bar (13). Upon this are loaded as many of the cast-iron weights (14, 15) as may be required. At the floor, the weight (consisting of 14, 15, 16, *etc.*) enters a vertical passage which extends to the basement floor, fifty-five feet below. The detachable wrench (16) is provided with extensions and is employed to raise the weight and coil the cable about the drum.

When the press is to be packed with clay, it is placed in a vise, and the "putty" is introduced in small quantities. After each addition, the material is tamped down with a stick of hard wood and a hammer. The wrench is then applied and given a turn from time to time until the water nearly ceases to run. Finally, the press is placed in its position as shown in Fig. III, and the weight is released.

We have no invariable rule which is to be followed in pressing the clay. Usually, however, it is subjected for about 14 or 16 hours to an estimated total pressure of 200 tons. If a smaller pressure is used, the duration of the pressing period must be increased. The sole guide in the matter is the conduct of the product when it is cut into shape on the lathe. It must be neither *too wet* nor *too dry*.

C. The Cutting of the Cells.

The cutting of the cells is a very critical operation, which requires not only experience but also highly developed mechanical instincts. Very few, even of those who have had mechanical training, ever succeed in the undertaking. The ex-

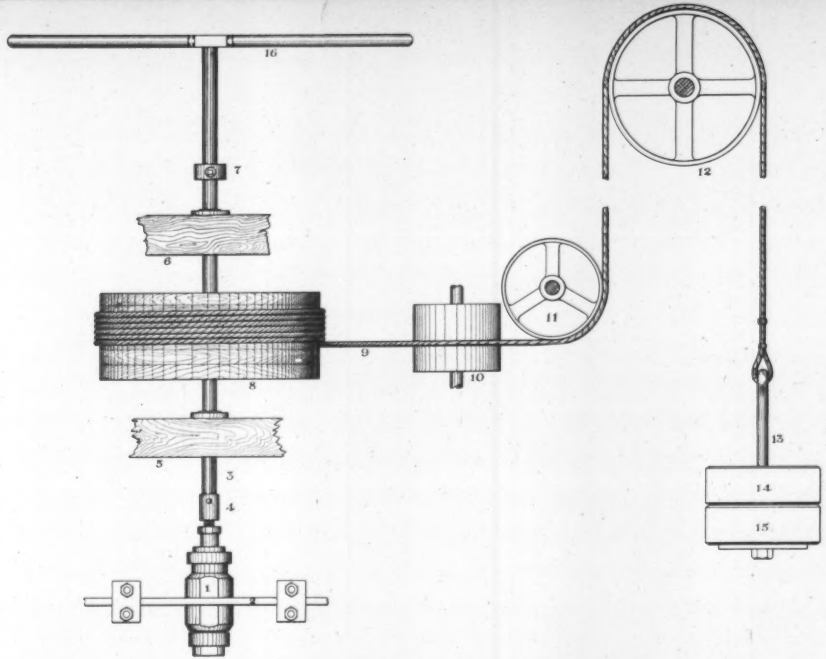


Fig. III

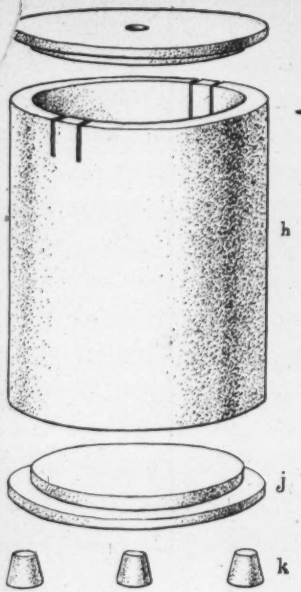


Fig. VII.

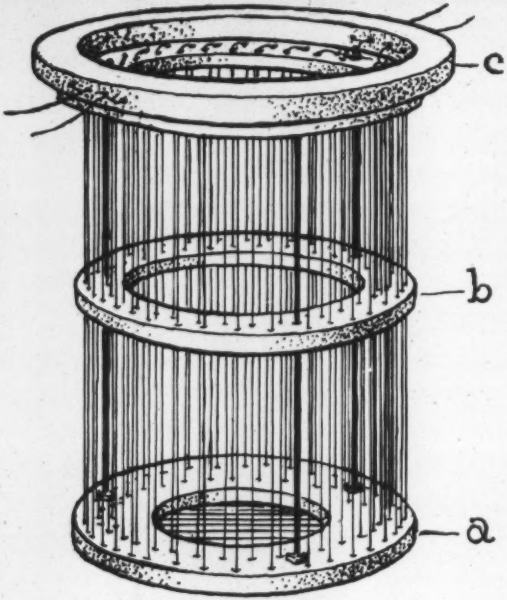


Fig. VI

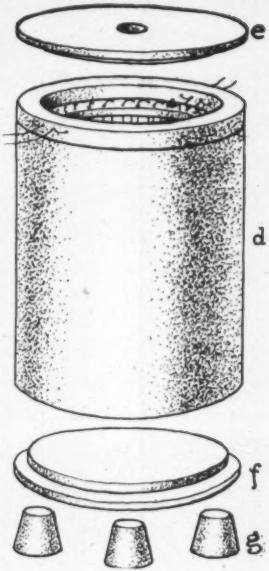


Fig. VIII.

planation of so many failures is very simple: *The cell wall must not be weakened at any point by the pressure of the cutting tools*; because, when the cell is baked, the shrinking material (the shrinkage is about 10 per cent.) necessarily draws away from places of relative weakness towards those where the cohesion of the particles is stronger, and *cracks* are developed. It is by no means necessary that the damage done by irregular pressure from the tools, or by too great pressure, should be obvious in the finished cell. In fact, it is rarely discovered until the cells are taken from the kiln. At first, our failures from the cause alluded to were over 90 per cent. At the present time, about 10 per cent. of the cells develop cracks while in the kiln. The improvement has been due, in a large measure, to improvements in the cutting tools and to the increased attention which has been given to keeping them in good condition. The usual lathe cutting tools were found to be ill-adapted to the work, and it was necessary to design others with new forms of cutting edge. But, however good in general the design of the tool may be, failure is bound to attend its use in this work unless the cutting edge conforms at all times to the principles which good mechanics *feel* and practice by, even when they do not understand them.

The cylinder of compact clay, as it comes from the press, is shown in Fig. IV. It is placed in a chuck of special design, and cut by tools, likewise of special design—and at a speed which the operator has found to be best adapted to his purpose—into the form shown in Fig. V. The many details of the operation are omitted because it is not believed that their publication in the fullest manner would lead to the manufacture of the much-needed supply of good osmotic cells, and because, to most of our readers, they would be unnecessary and irksome.

D. The Burning and Glazing of the Cells.

Nearly all of our experimental work in the baking of clays was for several years done in an electric kiln which was designed for the purpose. A description of it has been published elsewhere,[1] but we venture to reproduce the cuts of it

[1] THIS JOURNAL, **32**, 93.

here, in the first full account of the method of making cells, because of the important part it has played in the successful solution of that difficult problem. It is shown in Figs. VI, VII, VIII and IX. It will be seen to consist (Fig. VI) of platinum wires, threaded through three clay rings, which are held apart by three platinum rods. The rods expand in the same degree as the wires, and thus keep the latter always taut, whatever may be the temperature of the furnace. The wires are in two pieces of equal length, so that they may be placed in series or parallel, according to the amount of current which it is desired to use. Fig. VII shows the furnace in place in the innermost of the clay cylinders which surround it when in use. The other clay cylinder, the outer one, is shown in Fig. VIII. Fig. IX exhibits all the parts of the kiln in their mutual relations, though, as will be seen by the figures, the original drawing was made to illustrate the use of the instrument as a crucible furnace. The kilns (of which we had three in use) were all calibrated by means of a Le Chatelier pyrometer. They thus became, in themselves, *resistance pyrometers*, the temperature of which could be easily ascertained at all times. A Seger gas experimental kiln was also used at different times, especially when we were trying to develop a suitable glaze for the cells.

The electric kiln answered well every purpose for which it was constructed up to about 1200°, *i. e.*, to a temperature at which platinum begins to volatilize in an atmosphere containing oxygen. At higher temperatures, the loss of platinum from this cause was sufficient to make necessary a frequent recalibration of the kilns. Fortunately, when we were in trouble in consequence of this phenomenon, we were offered the free use of the kilns of the Chesapeake Pottery Co. by the late president of that concern, Mr. D. F. Haynes. At the pottery we could neither control nor know with certainty the temperature of any part of the kilns, but it was easy to find the places in them where the best results were most frequently obtained. Since then, all of the cells have been burned at the pottery.[1] In general, the hotter parts of the kilns, where

[1] It should be stated also that we are under great obligation to the superintendent of the Chesapeake Pottery, Mr. Thomas Mayer, for his friendly coöperation.

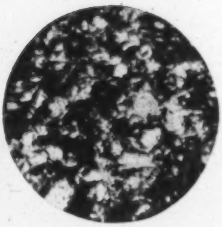


Fig. X.

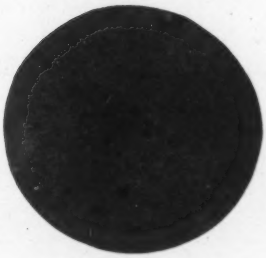


Fig. XI.

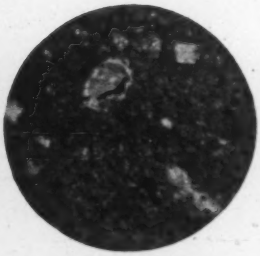


Fig. XII.

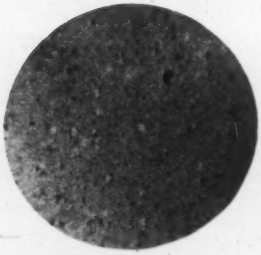


Fig. XIII.

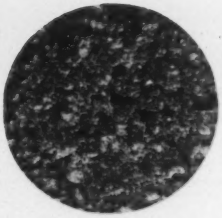


Fig. XIV.

Fig. XV.

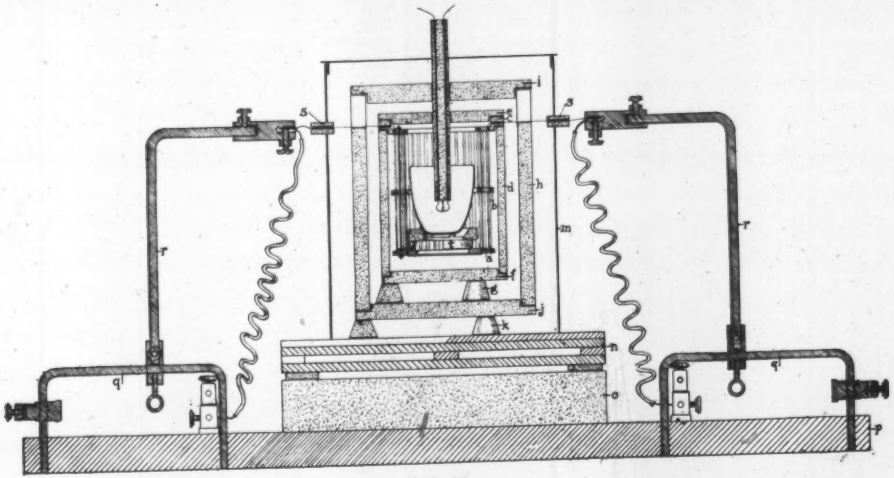


Fig. IX.

the temperature is certainly above 1200°, but probably somewhat under 1400°, are selected.

It has been stated elsewhere that in our endeavor to produce the correct texture of cell wall, we made a study of thin sections, both of the potters' cells and of our own products. In the course of this work a considerable number of photographs have been accumulated, six of which are here reproduced. Three of them (Figs. X, XII and XIV) are from potters' cells, and three (Figs. XI, XIII and XV) are from the first cells made by us which proved themselves well suited to the measurement of osmotic pressure. It will be noted that the texture of the cells made in the laboratory is incomparably finer (closer) than that of the potters' products. But we are convinced, after five years of laborious investigation, that just this *excessive fineness of texture* is absolutely *indispensable* to the correct measurement of osmotic pressure. It is necessary, in the first place, in order that the membrane may be deposited *exclusively upon the inner surface* of the cell wall; and it is necessary, also, in order to give the membrane a *backing* which will enable it to withstand pressure. If the texture is more open than that shown in Figs. XI, XIII and XV, the membrane is deposited, at least partially, *within* the wall, and it breaks under moderate pressure.

An explanation is called for of the numerous black specks which are seen upon Figs. XI, XIII and XV. They are particles of the emery which was used in grinding the sections, and no part of what the photographs are intended to show. Unfortunately for the progress of the work, we have been obliged to make excursions into many fields previously unfamiliar to us, and one of these was that of *microphotography*. This will accouut for any defects which an expert may detect, including a failure properly to cleanse the sections before photographing.

We are unable to state at the present time the exact extent to which the sections here reproduced were magnified, the orginal records having been mislaid or lost, but it is believed to have been 125 diameters.

The question naturally arises, whether it is possible to

make the texture of a cell wall *too close*. We cannot answer the question positively, but we are inclined to think that it is; for, in some cases where the cells had been baked at very high temperatures, and had, in consequence, suffered an unusual amount of contraction, it was found that the membranes would not adhere well to the walls. A tentative explanation is that the membrane, though deposited in general on the surface, must be *rooted* somewhat into the wall (the pores) in order to adhere to it firmly. This assumption appears to be in accordance with the little evidence which has been gathered through microscopic examination.

After baking the cells, and before glazing them, they are ground under the shoulder to fit the brass rings with which the manometers are fastened in place. The necks also are ground to the exact taper of the brass cones upon the ends of the manometers, a high speed carborundum wheel being employed for the purpose.

The finding of a suitable glaze for the upper half of the cells was a matter of considerable difficulty. As might have been expected, the expansion coefficient of products made as these cells are is very different from that of any of the potters' wares, hence none of the glazes which are used by the potters would meet our requirements. All such glazes were found to "craze" badly upon the biscuit. An attempt was made to glaze with feldspar, but with poor success. A wholly suitable glazing material was finally obtained by adding silica and feldspar to one of the glazes which is used by the potters on the better grades of their white table ware. The earlier experiments in glazing were carried out at the laboratory in a Seger gas kiln, but at the present time the cells are glazed at the Chesapeake Pottery.

There is one objection to glazing the cells, to which attention should be called. They are glazed, inside and outside, from the middle upwards. The whole of the interior surface of the cell is covered either by the glaze or by the membrane, so that no material in solution can diffuse into the cell wall from the inside. On the outside, the case is different; there it is quite possible for dissolved substances to diffuse

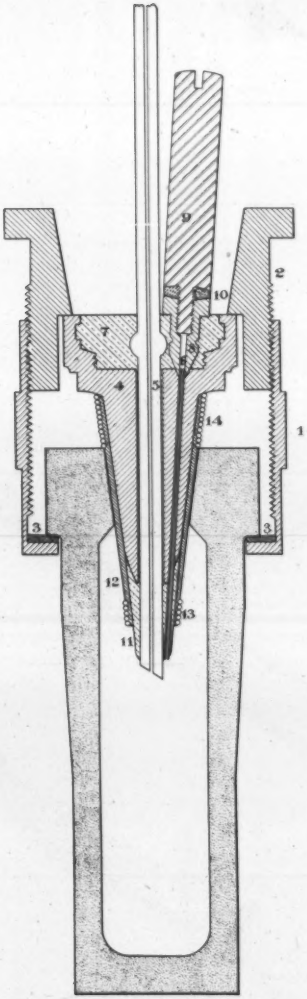


Fig. XVI.

in and to accumulate between the inner and the outer glazed surfaces. If these should afterwards diffuse downward and distribute themselves about the membrane, the pressure measured would evidently not be that of the solution within the cell, but the difference between the pressures of the two solutions on the opposite sides of the membrane. This possible vitiation of the results has been a source of much anxiety, and we have endeavored to guard against it by soaking the cells continuously, when not in actual use, in pure water which is frequently renewed. A radical remedy for the difficulty would be a cell, the upper half of which is entirely nonporous; and we have been endeavoring for the past three years to produce a cell, the upper half of which would become porcelain on baking, while the lower half remained porous and suitable for the deposition of a membrane. The results have not been wholly satisfactory up to the present time, but we do not yet despair of final success. The difficulty is, of course, that of producing clay mixtures for the two parts of the cell which shall maintain *identical expansion coefficients* throughout the whole of the baking and cooling periods; since otherwise cracks, or at least a condition of weakness, must develop at the junction of the two parts. This is believed to be the last of the many serious problems with which we have had to deal in the manufacture of osmotic cells.

E. The Manometer Attachments.

In 1908 we published a description[1] of the cell, with its manometer attachments, which was at that time in use. The improvements which have been made since then affect only the minor features, and none of them are of a radical character. They have nevertheless contributed materially to the ease and the accuracy of the measurements of pressure. Fig. XVI is intended to show every essential detail of the closed cell as it has been used throughout the recent work on the temperature coefficient of osmotic pressure. The function of the brass collar (1) and of the brass nut (2) will be readily understood without explanation. The form of these pieces

[1] This Journal, **40**, 266.

has varied but little during the past eight years. The lead ring (3) separates the shoulder of the cell from the flange of the brass collar and serves to protect the glaze upon the former. A ring of softer material than lead, *e. g.*, leather, cannot be used for the purpose, since any upward movement of the collar—due to diminishing thickness of the ring—would lead to an increase in the capacity of the cell and a dilution of the solution. In other words, the ring (3) must be of fairly rigid material. The brass cone (4) has two holes passing entirely through it, one for the manometer tube (5) and the other for the hollow needle (6), both of which (the manometer and the needle) are securely fastened in the cone by means of the Wood's metal (7). The holes through the cone are bored slightly larger than the tubes which are to occupy them, in order that the molten metal may flow down and completely fill the space between the latter and the walls of the former. In this way the tubes are fixed more firmly in their places, and all danger of leakage upwards through the cone is avoided. The hollow tube (6)—the needle—is nickel-plated and is brazed into the brass piece (8), which is bored out larger and threaded internally at the upper end to fit the closing plug (9). The upper end of (8) and the lower end of the larger portion of (9) are made concave in form, and between them is placed the grease-filled leather packing (10). The concave form of these two surfaces is essential, since it effectually prevents any outward lateral movement on the part of the packing and gives a tight joint under the highest pressures. After fixing the needle and the manometer tube (or rather, the tube which is to be fused to the manometer) in their places by means of the fusible metal, the cone (4) is extended by the Wood's metal seen at (11). The extension is for the purpose of covering and protecting the lower portion of the needle tube. Over the cone, thus lengthened by the Wood's metal, is slipped the rubber tube (12) which is tightly wound, at the lower and upper ends, with twisted shoemakers' thread (13, 14). Owing to the ease with which rubber always moves towards a region of smaller pressure, the whole space (14) between the shoulder of the brass cone

and the top of the cell must be covered and rigidly supported by the thread. In practice, the winding of the upper end of the rubber tube is carried so far down that the last two or three turns of the thread are actually within the neck of the cell when it is closed for a measurement of pressure.

A manometer, on whose calibration and verification weeks, and perhaps months, of labor have been bestowed, is too precious an instrument to be unnecessarily exposed to danger. Hence the cones are not attached in the first instance to the manometers, but always to short pieces of tubing of the same kind, which are afterwards fused to the manometers or cut off from them, as occasion may arise.

The finished cell, as described above, is satisfactory in all respects, except in the one particular already alluded to, namely, that there is a *chance* that dissolved matter may diffuse in between the two glazed surfaces and afterwards affect the measurement of pressure in the manner which has been explained. It is not believed, however, that any of our results have been vitiated in the slightest degree from such a source. Nevertheless, it would give us great satisfaction to remove the danger altogether by making a cell half porous and half porcelain, which would not require glazing; and it is in this direction only that any further improvement of the cell is anticipated.

JOHNS HOPKINS UNIVERSITY,
Dec. 1, 1910.

THE ABSORPTION SPECTRA OF CERTAIN SALTS OF COBALT, ERBIUM, NEODYMIUM AND URANIUM AS AFFECTED BY TEMPERATURE AND BY CHEMICAL REAGENTS.[1]

BY HARRY C. JONES AND W. W. STRONG.

PART II.

Introduction.

In the absorption spectra of salts in solution, very few of the salts having characteristic banded spectra show much,

[1] The first part of this article was published in THIS JOURNAL, **45**, 1.

if any, influence of the acid radical. In the case of uranium salts there are, however, several exceptions. One of these is the aqueous solution of the nitrate and the other salts. The nitrate bands have been shown to have shorter wave lengths than those of the other salts. In the following description a detailed account will be given of the changes of the spectra as the nitrate is gradually changed into the sulphate or the chloride.

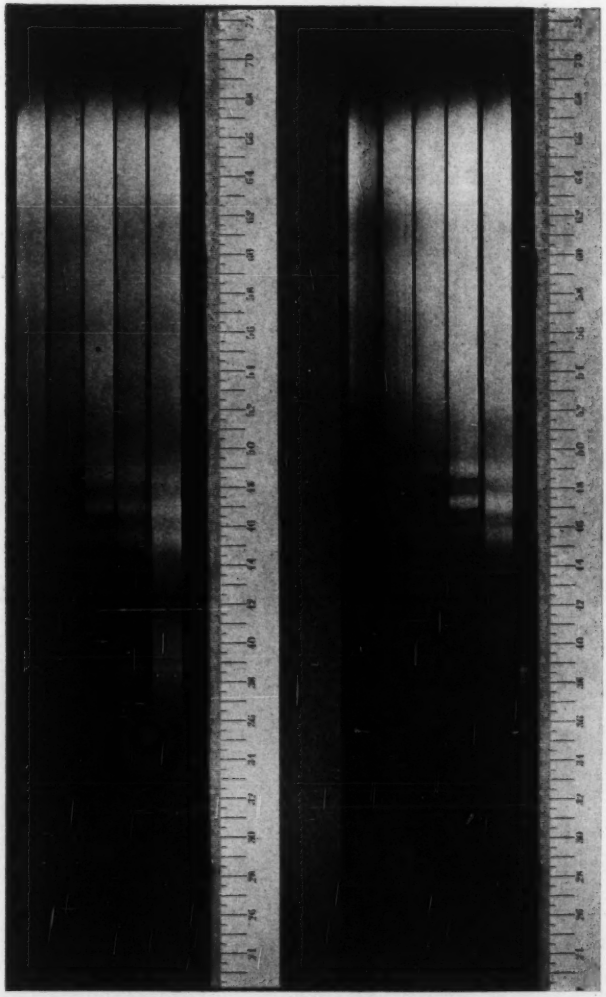
Spectrophotography of Chemical Reactions of Uranyl Salts.

In Plate VIII is shown the absorption spectrum of an 0.08 normal solution of a uranyl salt in water 15 mm. in depth. Beginning with an 0.08 normal solution of uranyl nitrate, sulphuric acid was added so as to make the concentration of acid, beginning with strip 1, as follows: 0.37, 0.73, 1.46, 2.92, 5.84, 10.22, and 14.60 normal.

In strip 1 there is practically the sulphate spectrum, most of the nitrate having been transformed. The addition of more acid does not produce any marked change until we reach the sixth and seventh strips. The *c* and *d* bands are very

	Nitrate bands.	Sulphate bands.	Strip 1.	Strip 5.	Strip 6.	Strip 7.
				5230?		
				5200?		
				5170?		
				5100?		
				5000?		
a	4890	4900	4900 to 5100	4910	4920	4920
	4800					
b	4742	4740	4730	4750	4740	
	4722					
c	4540	4580	4570	4570	4570	4550
d	4390	4460	4440	4450	4480	
e	....	4330	4320	4340	4340	4370
f	4155	4200	4200	4200	4210	4225
g	4030	4070	4070	4070	4080	4090
h	3905	3970	3950	3970	3960	3970
i	3815	3850	3850	3850	3860	3860
j	3710	3740	3720	3740	3750	3760
k	....	....	3620	3620	3640	3650
l	3515	3530	3520	3520	....	....

Plate VIII.



A B

greatly shifted, so that in the latter strip they form a single band. Several of the other bands are considerably shifted towards the red. Throughout the changes of conditions above named, the bands remain quite sharp and well defined (for uranyl bands), and change very little in intensity. This is in quite marked contrast with many of the plates in which there are certain stages that hardly show any uranyl bands at all, whereas at other stages the bands are very strong indeed.

The bands in the upper strips beyond the region λ 5000 are probably due to nitric oxide. Several of the bands are quite strong.

The simplest interpretation of this plate is that as more and more sulphuric acid is added molecules are formed that contain more and more of the acid. That there are several of these compounds formed seems probable, since the shift of the bands is quite large and this shift takes place gradually.

	Nitrate bands.	Chloride bands.	Strip 1.	Strip 6.	Strip 7.
a	{4890 / 4800}	4920			
b	{4742 / 4722}	4740	4700 weak and broad	4720	4740
c	4540	4560	4560 weak and broad	4580	4580
d	4390	4460	4410 weak and broad	4430	4440
e	....	4315	4270 strong	4280	
f	4155	4170	4140 strong	4145	
g	4030	4025	4020 strong	4020	
h	3905	....	3900	3900	3900
i	3815	....	3800	3800	
j	3710	....	3700	3700	3700 weak
k	....	....	3600	3600	3600 weak
l	3515	....	3500	3500	

Plate XIII, *A*, shows the effect of adding sulphuric acid to an aqueous solution of uranyl nitrate. The first strip here gives the absorption of uranyl nitrate to which no acid has been added. The changes here are from the neutral nitrate bands to the neutral sulphate bands, approximately. There is in this case a gradual shift of the bands to the red.

The effect of adding hydrochloric acid to an aqueous solution of uranyl nitrate was studied. The depth of cell was

15 mm. The concentration of the uranyl salt was kept constant. The percentages of acid were increased.

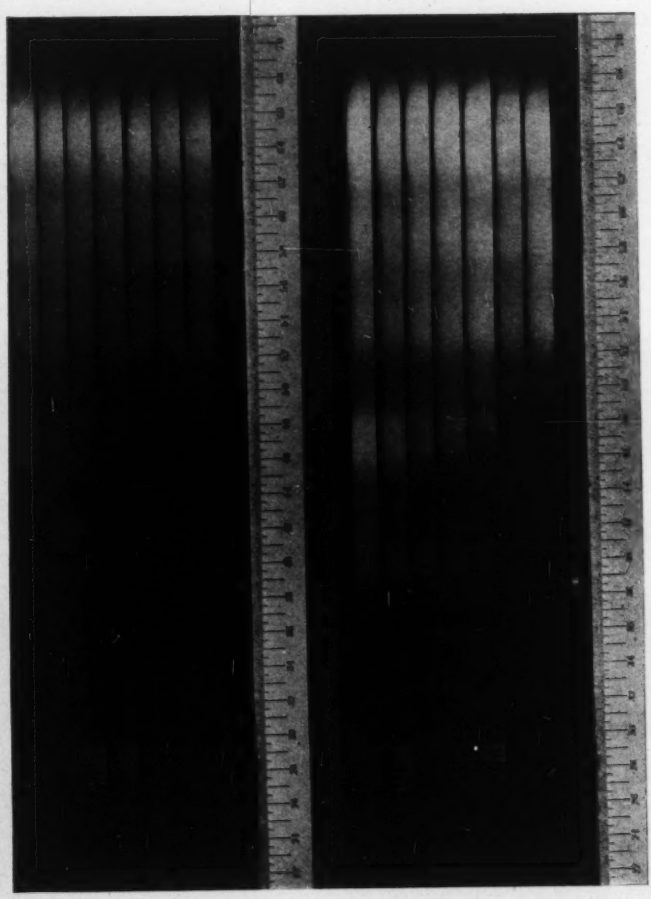
In the first strips of the spectrograph the *b* and *c* bands are very weak. They become stronger and shift gradually to the red. The other bands are quite sharp until the last strip, where they appear very weak. Their wave lengths are but slightly changed. In the above table the wave lengths of the neutral chloride and nitrate bands are taken from the other tables.

Plate XIII, *B*, represents the absorption spectra of uranyl nitrate to which acetic acid had been added. Plate XII, *A*, represents the same effect, except that here the original uranyl nitrate solution was only 1 mm. in thickness, so that the ratio of acetic acid to the amount of uranyl salt was much larger.

	Uranyl nitrate.	Strip 1. Plate XIII, B.	Strip 6. Plate XIII, B.	Strip 1. Plate XII, A.	Strip 3. Plate XII, A.	Strip 5. Plate XII, A.	Uranyl acetate.
a	{4890 / 4800}	4830?					
b	{4742 / 4722}	4660	4675			4860	4900
c	4540	4510	4520		4650	4720	4770
d	4390	4370	4380	4420 weak	4500	4570	4600
e	....	4245	4250	4270	4350	4440	4460
f	4155	4130	4140	4150	4220	{4340 / 4220}	4320 / 4200
g	4030	4020	4030	4020	4030	4120	4090
h	3905	3910	3920	3910	3910	4010	3975
i	3815	3800	3810	3800		3870	
j	3710	3670	3700	3700		3770	
k	....	3570	3580	3600		3670	
l	3515	3460	3460				

The first effect which the addition of acetic acid produces is to shift slightly the uranyl bands of the nitrate to the red, and to cause them to become much sharper. When some twenty times as much strong glacial acetic acid had been added as was equivalent to the uranyl nitrate solution, the uranyl bands became quite weak, and shifted very greatly towards the red, as is shown in Plate XII, *A*. The *e* and *f* bands are each shifted nearly 200 Angström units. When

Plate IX.



A B

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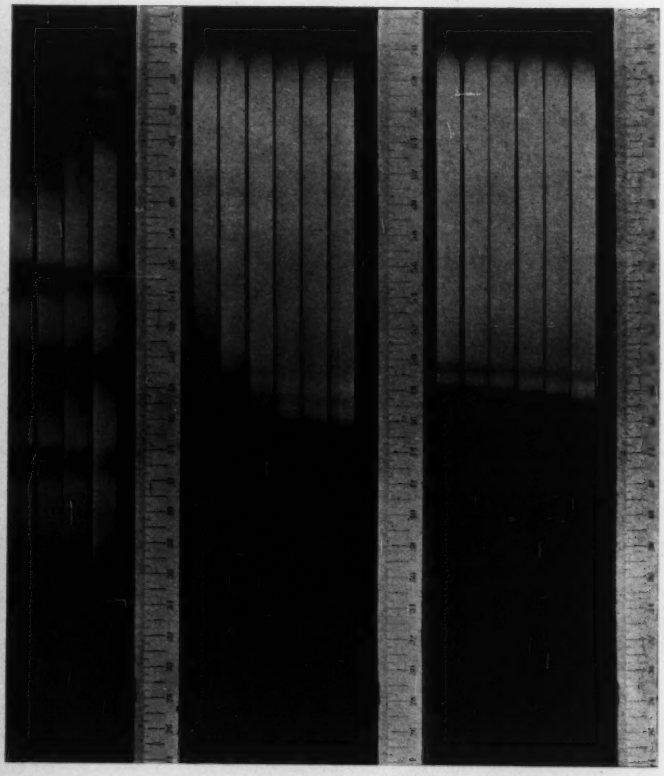
Plate X.



A B C

this enormous shift towards the red takes place a *new* band appears between *f* and *g*. This new band will be called f_1. Further addition of acetic acid causes the uranyl bands to become stronger again, producing at the same time a small shift to the red.

Uranyl Chloride in Glycerol.

Plate IX, *A* and *B*, represents the absorption spectra of a solution of uranyl chloride in glycerol, the depths of cell being 10 and 5 mm., respectively. The concentrations, starting with the strip nearest the scale, were 0.176, 0.132, 0.088, 0.059, 0.041, 0.032, and 0.022 normal. The spectrograms are very similar to those of the other uranyl salts. The blue-violet absorption band vanishes at about λ 4300. The positions of the uranyl bands are: *a*, 5050; *c*, 4720; *d*, 4540; *e*, 4400; *f*, 4260; *g*, 4140; *h*, 4025; and *i*, 3920.

The uranyl bands of a glycerol solution are quite broad. The same is true of the uranous bands. Glycerol usually has the effect of making the bands less dense than they appear for most of the other solvents. In a few cases the bands are quite fine, however, as in the case of the erbium and neodymium salts.

Uranous Salts.

Uranium was discovered in 1789 by Klaproth and was named to commemorate the discovery of the planet Uranus by Herschel in 1781. Quite a large number of oxides are known.

The orange oxide, $UO_3(UO_2O)$, or uranyl oxide, is obtained by heating uranyl nitrate slowly as long as acid fumes escape. When the nitrate is rapidly decomposed a red modification of the oxide is produced. All the uranyl salts may be considered as compounds of UO_3 where one of the oxygen atoms has been replaced by an acid or halogen radical. Aqueous solutions of the uranyl salts are partly hydrolyzed. The nonhydrolyzed portion dissociates in the usual way.

Urano-uranic oxide, U_3O_8, is obtained by heating uranyl nitrate to a high temperature.

The oxide UO_2 is obtained by heating the oxide U_3O_8 in a

current of hydrogen, and is of a brown or copper-red color. The reduction of an oxide of uranium to the oxide UO_2 and weighing is an analytical method of estimating uranium. This oxide in acid solutions forms the green uranous salts.

The oxide U_2O_5 is formed when ammonium uranate is strongly ignited in air. The oxide UO_4 is formed when a dilute solution of hydrogen peroxide is added to uranyl nitrate. The uranates have the general formula $R_2U_2O_7$, as, for example, potassium uranate, $K_2U_2O_7$. When alcohol is added to a solution of hydrogen peroxide, uranyl nitrate, and sodium hydroxide (a minimum amount of the hydroxide), golden yellow needles crystallize out having the composition $(NaO_2)_2UO_4.8H_2O$.

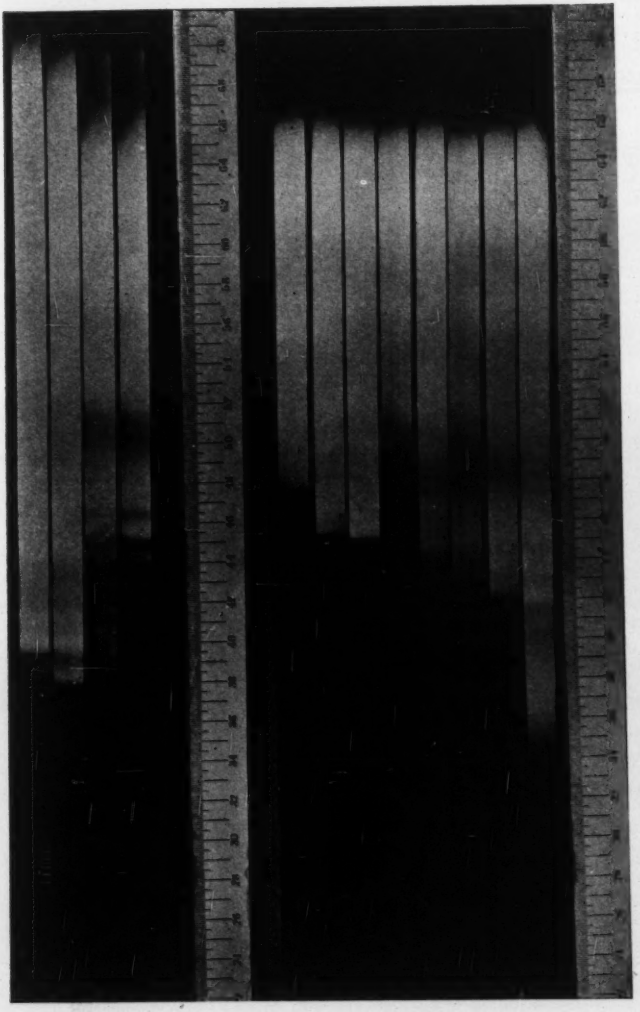
Very little work has been done up to the present on the absorption spectra of uranous salts, largely because of their very unstable character in solution. J. Formánek describes the absorption spectra of uranous chloride. This was prepared by adding a little zinc and hydrochloric acid to a uranyl chloride solution. He found that the spectrum changed as the uranyl chloride was being reduced. A very strong band was found at λ 6507. The other bands, eleven in number, were $\lambda\lambda$ 6722, 6367, 6165, 6030, 5782, 5497, 5238, 5064, 4962, 4840, and 4519.

A similar method has been used by the authors. The uranous nitrate, sulphate, and chloride were formed by adding the corresponding acid to a solution of the uranyl salt containing some zinc. The uranous chloride and sulphate were quite stable in solution, remaining reduced for weeks. Uranous sulphate crystallizes out from solution as $U(SO_4)_2.9H_2O$. Solutions in alcohol can be reduced just as easily as solutions in water. Uranous nitrate was found to be very unstable. At the present writing a number of spectrograms have been made, and much more work will be done on these uranous salts and on the absorption spectra of the various oxides. It has already been found that uranous chloride has very different spectra in different solvents.

Uranous Chloride in Water.

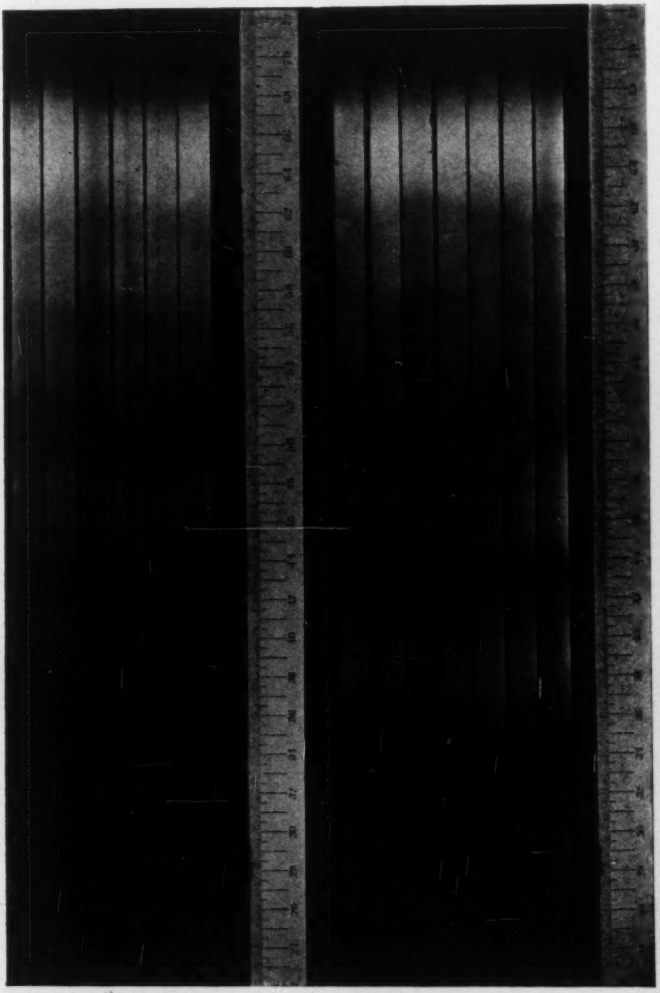
A solution of uranous chloride in water was made in the

Plate XI.



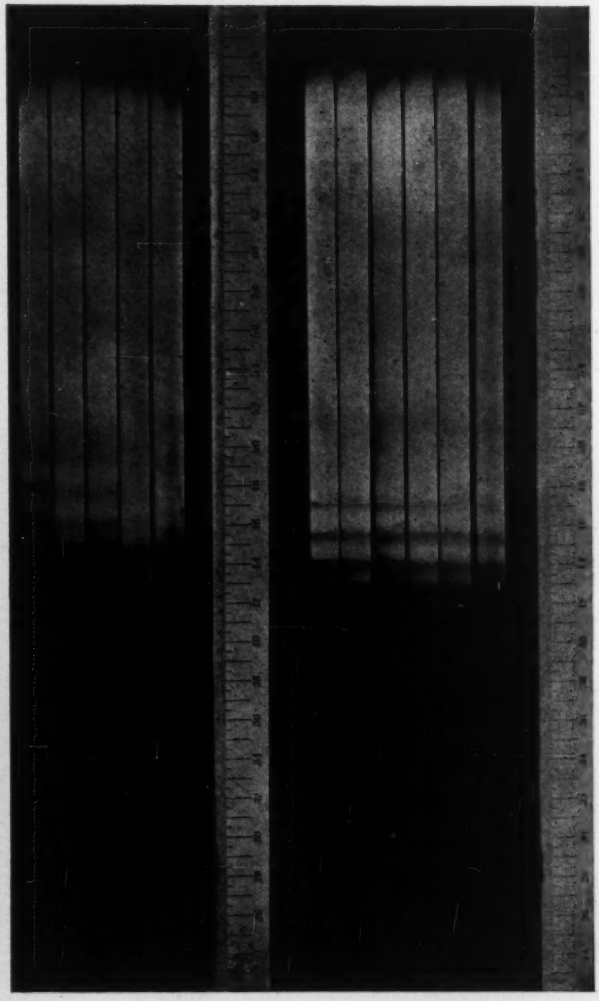
A B

Plate XII.



A B

Plate XIII.



A B

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usual way. This solution was of a dark green color even when very dilute. When sufficiently dilute most of the uranous salt came down as a precipitate after standing for several days. The solution was examined spectroscopically, it being practically colorless to the naked eye. The absorption spectrum corresponded closely to that of the uranyl chloride bands of water. The bands *e*, *f*, and *g* appear with considerable intensity, while the other bands are very weak, *e* consisting of two bands of about equal intensity and very close together. The wave lengths of the bands are approximately as follows: λ 5030 (weak); *a*, λ 4910; *b* (very weak), λ 4790; *c* (very weak), λ 4550; *d* (very weak), λ 4420; *e*, $\lambda\lambda$ 4305, 4270; *f*, λ 4150; and *g*, λ 4020.

The spectrogram (Plate XIV, *A*) represents the absorption of a 0.17 normal solution of uranous chloride in water. Starting with the first strip the depths of cell are 1.2, 2, 4, 8, 16 and 32 mm. For the first three strips the exposures were for 3 minutes to the Nernst glower for all the spectrum, 3 minutes to the ultraviolet, and 1 minute to the spark. The other three strips were exposed to the Nernst glower for 3 minutes. The slit width was 0.15 mm. and the current in the glower 0.9 ampere. No exposure to the ultraviolet was made for the upper strips, as it was considered that this region would be entirely absorbed. The spectrogram shows, however, that this would not have been the case.

Strip 1 shows complete ultraviolet absorption up to about λ 3300. Two absorption bands, $\lambda\lambda$ 4200, 4400, almost merge into each other. Of these the one with shorter wave length (λ 4270) is considerably stronger than the other (λ 4370). A strong band appears at λ 4980, about 30 Angström units wide. This is limited by a wide region of general absorption, which widens out very rapidly towards the violet with increasing depth of cell. This is most likely due to the presence of diffuse bands in his region. The diffuse band at λ 5500 widens symmetrically with increasing depth of cell. There are two very strong bands which for 2 mm. depth of cell are situated at λ 6430 to λ 6620 and λ 6720 to λ 6770. This region of absorption is a very characteristic one for uranous chloride

in water. Other diffuse bands appear at λ 3910, λ 4030, λ 4600, and λ 6340.

Uranous and Aluminium Chlorides in Water.

Uranyl chloride was reduced in the presence of an aluminium chloride solution of about 2.4 normal concentration. The concentration of uranous chloride was 0.17 normal. Plate XIV, *B*, represents the absorption spectrum, the depths of cell being 1.2, 2, 4, 8, 16 and 32 mm.

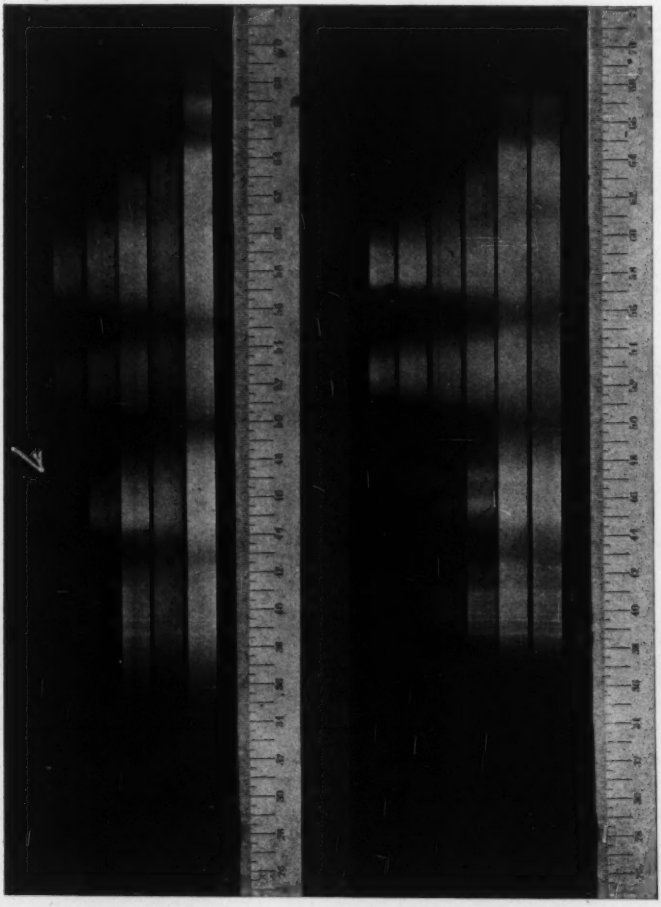
The resulting spectrum is very much like that of the pure aqueous solution. The ultraviolet absorption is much greater, the absorption extending to about λ 3800. The presence of aluminium brings out several bands in the blue-violet region which we shall continue to designate as the uranyl bands. These bands have the same wave lengths as the corresponding uranyl bands of a solution of uranyl and aluminium chlorides in water.

The band at λ 5000 is much more diffuse than the corresponding band for water. The band at λ 5570 widens symmetrically with increasing depth of cell. Besides these bands there are two bands at λ 6550 to λ 6640 and λ 6750 to λ 6800. The general effect of the aluminium chloride is to bring out the uranyl bands; to increase the ultraviolet absorption; to make the band λ 5000 and others slightly more diffuse and to cause the uranous bands to shift towards the red, about 20 or 30 Angström units.

The concentration of uranium in a solution necessary to bring out the uranyl bands either in the uranyl or uranous condition is about the same.

The spectrogram, Plate XXIV, *A*, shows the effect of the presence of aluminium chloride and hydrochloric acid upon the uranous bands. Strip 1 represents the absorption of a 0.17 normal solution of uranous chloride in water 3 mm. deep; strip 2 the same, to which a 3.04 normal solution of aluminium chloride had been added, so as to make the depth of cell 4 mm.; strip 3, a depth of cell of 6 mm.; strip 4 represents the same as strip 1; strip 5 shows the absorption of the solution of strip 4, to which sufficient hydrochloric acid had been added to make a depth of cell of 16 mm. Both alumin-

Plate XIV.



A B

ium chloride and hydrochloric acid cause the ultraviolet absorption to increase very much. Aluminium chloride has much the same effect as hydrochloric acid, although not so great. It does not change the water bands λ 6400 and λ 6655 as does hydrochloric acid. Strip 3 shows bands at the following positions: *g*, λ 4140; *f*, λ 4280 (strong); *e*, λ 4400 (*e* and *f* almost merge into each other); *d*, λ 4490; *c*, λ 4620; *b*, λ 4780, λ 4990, λ 5550, λ 6460 to λ 6660, λ 6780.

Two cc. of a normal aqueous solution of uranyl chloride were added to 8 cc. of a 3.04 normal aqueous solution of aluminium chloride and to this were added 2 cc. of hydrochloric acid and zinc, so that the uranyl salt was reduced to the uranous condition. To a 2 mm. depth of solution was added water so as to make the depth of cell 7 mm. The addition of water caused the *b*, *c*, *d*, and *e* bands to become very faint and to be shifted to the violet. The band at λ 4980, and especially the bands at λ 5500, λ 6500, and λ 6750 were very considerably shifted. The solution of 7 mm. thickness showed bands at $\lambda\lambda$ 4130, 4210 (narrow), 4285, 4420(?).

Uranous Chloride in Acetone.

Plate XVII, *A*, strip 1, represents the absorption of a 1.8 mm. solution of uranous chloride in acetone, the solution having been made about 2 weeks before using; strip 2 represents the absorption of the same solution to which 0.5 mm. hydrochloric acid had been added; strip 3 the same as 1 to which 1.2 mm. of hydrochloric acid had been added (in this case a small amount of a brown precipitate was formed causing the absorption to be greatly increased); strip 4 represents an ether solution (ether was added to the acetone solution of uranous chloride, a deep green precipitate was formed and the ether became yellow) probably of uranyl chloride; strip 5 represents the absorption of an acetone solution of uranous chloride, freshly prepared, 2 mm. in depth; strip 6, the same, 5 mm. in depth; and strip 7, 14 mm. in depth.

The freshly prepared uranous chloride solution (in acetone) shows the uranous bands very faintly. The addition of hydrochloric acid is seen to bring out the bands very well.

In addition to the bands already described, faint bands (strip 2) appear at λ 6090, λ 6340, λ 6365, and λ 6390. The ether bands occur as follows: *a*, λ 4930; *b*, λ 4760 (a faint component at λ 4800); *c*, λ 4600; *d*, λ 4440; *e*, λ 4290; *f*, λ 4155; g, λ 4030. The shifts of the ether bands relative to the bands of the solution of uranous chloride in hydrochloric acid are very noticeable when the spectrograms are made to overlap. With reference to these bands the ether bands *d*, *e*, *f*, and g are shifted to the red and the *a* and *b* bands to the violet.

Uranous Chloride in Hydrochloric Acid and Acetone.

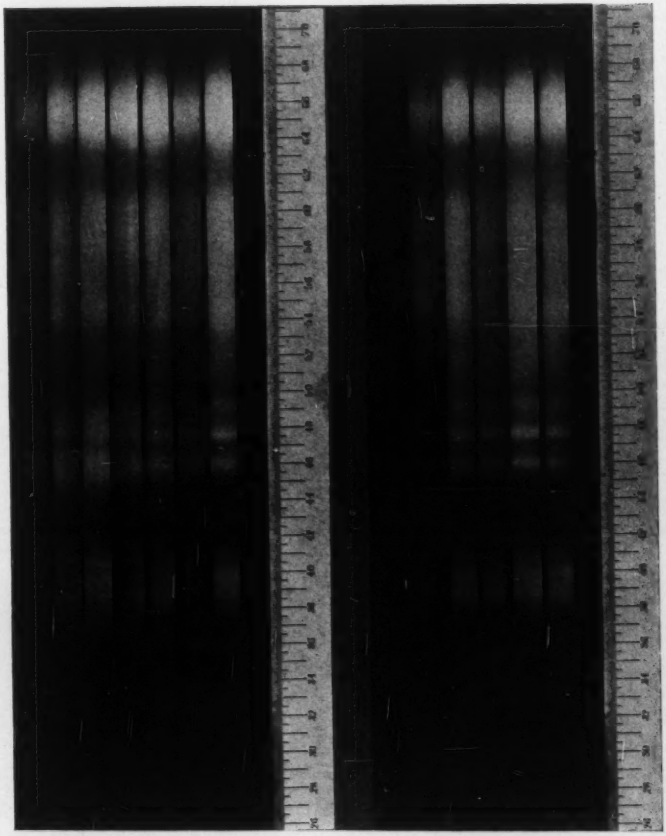
A 0.2 normal solution of uranyl chloride in strong hydrochloric acid was reduced by using as little zinc as possible. A plate showing the absorption spectra of this solution to which acetone has been added was made. Strip 1 represents the absorption of 5 mm. of the hydrochloric acid solution; strip 2 the same, to which 1 mm. of acetone has been added; strip 3, 3.3 mm. acetone; and strip 4, 12 mm. of acetone. The solution was thoroughly mixed in each case.

	Strip 1.	Strip 4.
a	4980 (100 A. U. wide)	4925(20)
b	4800	4760(20)
c	4620	4590(s) 4535(15)
d	4410	4425(s) 4470(f 20) 4380(f 20)
e	4280	4290(s) 4340(w20) 4240(w20)
f	4140	4160(s) 4200(w20) 4115(w20)
g	4010	4040

In strip 1,[1] *a* consists of a strong broad band. As acetone is added this breaks into two components, the component of longer wave length disappearing as more and more acetone is added. In strip 1 there is a very diffuse band near the *d* band on the long wave length side. In addition to the uranyl bands there is a broad band at λ 5550; one from λ 6450 to λ 6680; and one from λ 6720 to λ 6820. In strip 4 all the broad uranous bands have disappeared and there remain only fine bands from 10 to 20 Angström units wide. These were located at $\lambda\lambda$ 6780, 6740, 6690, 6625, 6600, 6555, 6490, 6470, 6040, 6000, 5960, 5910, 5220, 5210, and 5195.

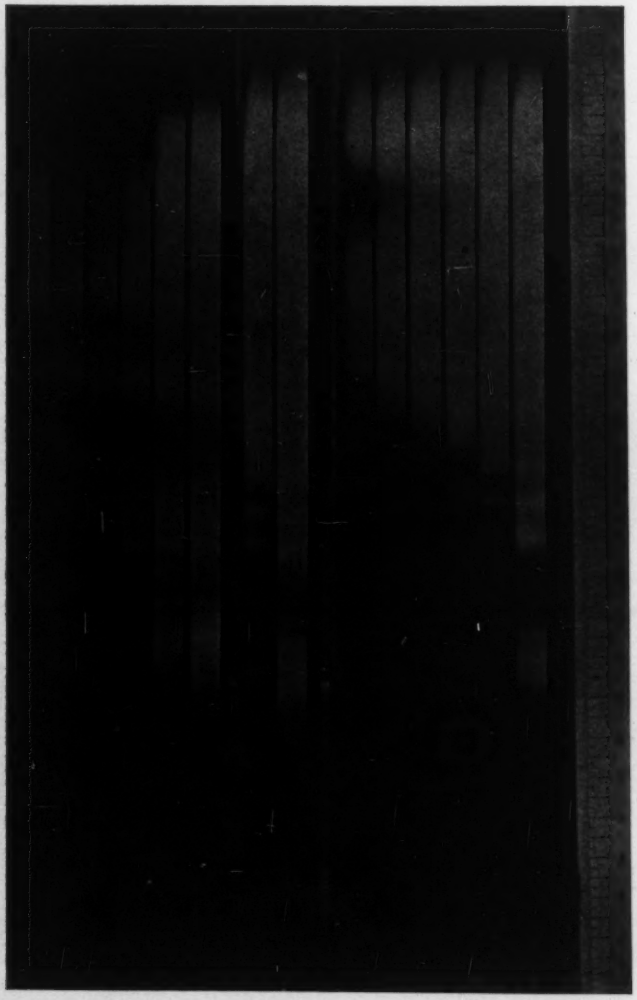
[1] For this and other plates not reproduced in this paper see Publication No. 130 of the Carnegie Institution of Washington, by the authors of this paper.

Plate XV.



A B

Plate XVI.



A B C

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Uranous Chloride in Mixtures of Methyl Alcohol and Water and of Methyl Alcohol and Acetone.

A plate was made showing the absorption spectra of a constant amount of uranous chloride in mixtures of methyl alcohol and water (*A*), and of mixtures of methyl alcohol and acetone (*B*), the lower strip representing the methyl alcohol solution.

As the amount of water increases, the water band λ 6750 comes out gradually. The methyl alcohol band λ 5050 to λ 4850 is probably double. This narrows on the red side into a band at λ 4850. The methyl alcohol bands λ 4770 and λ 4600 practically disappear, and the band λ 4670 becomes very weak. In their places appear the water bands λ 4700 and λ 4550. The *de* band, λ 4300 to λ 4450, of the methyl alcohol solution weakens and breaks up, giving the *d* band at λ 4400 and the *e* band at λ 4280. This *e* band is a broadened band otherwise similar in appearance to the band λ 4300 in methyl alcohol, which appears quite narrow. The methyl alcohol bands *f*, λ 4230, and *g*, λ 4120, become the *g* water band at λ 4160, apparently by going together.

The most important change produced by adding acetone to a methyl alcohol solution of uranous chloride is to bring in a lot of narrow acetone bands in the region λ 6000 to λ 6500, and the strong absorption band from λ 6500 to λ 6800. There also appears a band at λ 5600.

Uranous Chloride in Water and Ethyl Alcohol.

The addition of ethyl alcohol (spectrogram XXIII, *A*) to an aqueous solution of uranous chloride causes a very marked change in the absorption spectrum, the water bands gradually disappearing and being replaced by ethyl alcohol bands. The spectrogram shows the decrease of intensity of the water bands very well. Strip 2 represents a 3.2 mm. depth of uranous chloride in water; 3 the same to which 1.2 mm. of ethyl alcohol has been added; 4, the same as 3, to which 2.2 mm. of ethyl alcohol has been added; 5 is the same as 4, plus 6 mm. ethyl alcohol; 6, the same as 5, plus 10 mm. ethyl alcohol. The upper strips are weak on account of the formation of a precipitate.

Uranous Chloride in Acetone and Water.

A plate was made showing the absorption spectra of uranous chloride in mixtures of acetone and water, *A* representing the more dilute solution of uranous chloride. The lower strip represents the absorption of an almost pure acetone solution, the other strips representing the absorption of the same solution to which greater and greater amounts of water are added.

This spectrogram shows that several of the uranyl bands are characteristic of acetone and aqueous solutions. The absorption of an acetone solution in the region λ 6500 is much less and consists of but a single band. The aqueous solution, on the other hand, has a very characteristic band at λ 6750. The band at λ 5550 of the acetone solution is shifted towards the violet as water is added.

As the percentage of acetone is decreased the acetone bands, *a*, λ 4920, *b*, λ 4750, and *c*, λ 4590 gradually disappear, while the water bands *a*, λ 4980, *b*, λ 4700, and *c*, λ 4570 gradually increase in intensity. No shift is to be noticed.

The other uranyl bands appear but slightly changed, the positions and intensities of the acetone and water bands being about the same. For the acetone solution they are *de*, λ 4430; *f*, λ 4290; *g*, $\lambda\lambda$ 4160, 4130; *h*, $\lambda\lambda$ 4040, 4010; and *i*, λ 3910. For the aqueous solution they are *de*, λ 4450 (weak), *f*, λ 4290; *g*, λ 4150; and *h*, λ 4010.

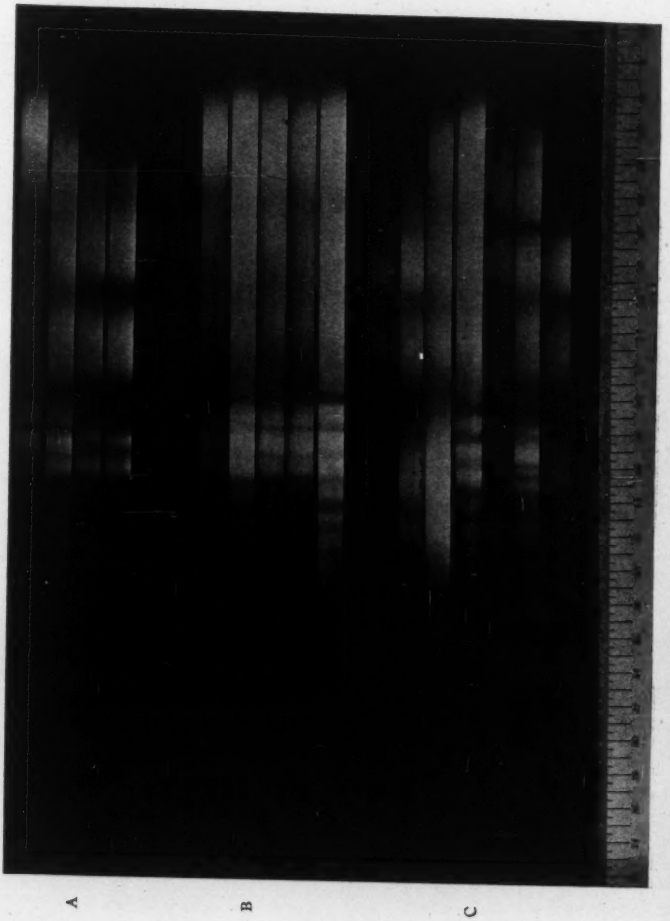
Uranous Chloride in Methyl and Ethyl Alcohols.

In the spectrogram, *A* represents the absorption of a dilute solution of uranous chloride in ethyl alcohol, and *B* in methyl alcohol. The depths of cell were 3, 6, 12, 24 and 35 mm., slit width 0.15 mm., exposure to Nernst glower 1.5 minutes to the whole spectrum, 2 minutes to the ultraviolet of the Nernst glower, and 1 minute to the spark.

The absorption of the two solvents is very much the same, the bands being much alike in intensity and position. The methyl alcohol bands are of slightly shorter wave lengths.

Ethyl alcohol solution: λ 4290 (narrow), λ 4710, λ 4950 to λ 5050, λ 5280 (weak), and λ 6200 to λ 6300.

Plate XVII.



Methyl alcohol solution: λ 4000, λ 4130, λ 4250, λ 4290 (narrow), λ 4700, λ 5020, λ 5260, and λ 6150 to λ 6300.

A solution of uranous chloride in methyl alcohol stood for almost a year. The absorption of this solution was quite different from that described above. This was probably due to the much larger amount of hydrochloric acid and zinc chloride in the old solution, as small amounts of hydrochloric acid as possible having been used in the solution described above. The positions of the bands of the "old" solution were: λ 3910 (double), λ 4020 (double), λ 4130 (double), λ 4590, λ 4750, λ 4710, λ 5000, λ 5550, and λ 6500 to λ 6800.

Uranous Chloride in Glycerol.

To make a glycerol solution of uranous chloride a strong solution of uranous chloride is made in some other solvent and is then mixed with glycerol and warmed. The warming is continued until as much as possible of the other solvent has evaporated. Spectrograms were then made with different depths of this solution, and of solutions in mixtures of glycerol with some other solvent. Plate XVI, *C*, represents the absorption spectra of a glycerol solution of uranous chloride of different depths; starting with the lowest strip the depths are 3, 4, 6, 9, 12, 18 and 24 mm. As the reduction was not complete it is impossible to know the concentration of the uranous chloride, although this could be found approximately. The spectrogram shows the uranyl bands and the uranyl blue-violet band. Knowing the depth of layer and having made the spectrogram it is possible to determine quite accurately the amount of uranyl chloride in the solution. The remainder of the uranium chloride is probably in the uranous condition.

The uranyl bands, *i*, λ 3800, *h*, λ 3930, and *g*, λ 4050, are very weak and about 60 Angström units broad. The band *f*, λ 4170, is fairly strong, as is also *e*, λ 4310; *d* is double, consisting of a wide diffuse band at λ 4440 and a narrower diffuse band at λ 4530; *c*, λ 4680, and *b*, λ 4840, are both very strong, and about 80 Angström units wide; *a*, λ 4980, is very narrow and has a very weak band at about λ 5060. The weak band at λ 5060 is barely visible in the original negative. For the greater depths of cell, bands several hundred Angström units

wide and extremely diffuse appear at about λ 5300, λ 5600, and λ 6300. These will be more fully discussed when uranous chloride in mixtures of glycerol and other solvents is discussed.

Uranous Chloride in Mixtures of Glycerol and Water.

The spectrogram, Plate XV, *A*, represents the absorption of a solution of uranous chloride in glycerol to which water is added. Strip 1 represents the absorption of a 6 mm. solution of uranous chloride in glycerol; the other strip shows the effect of adding water, the amount of water added being very small for the first few strips.

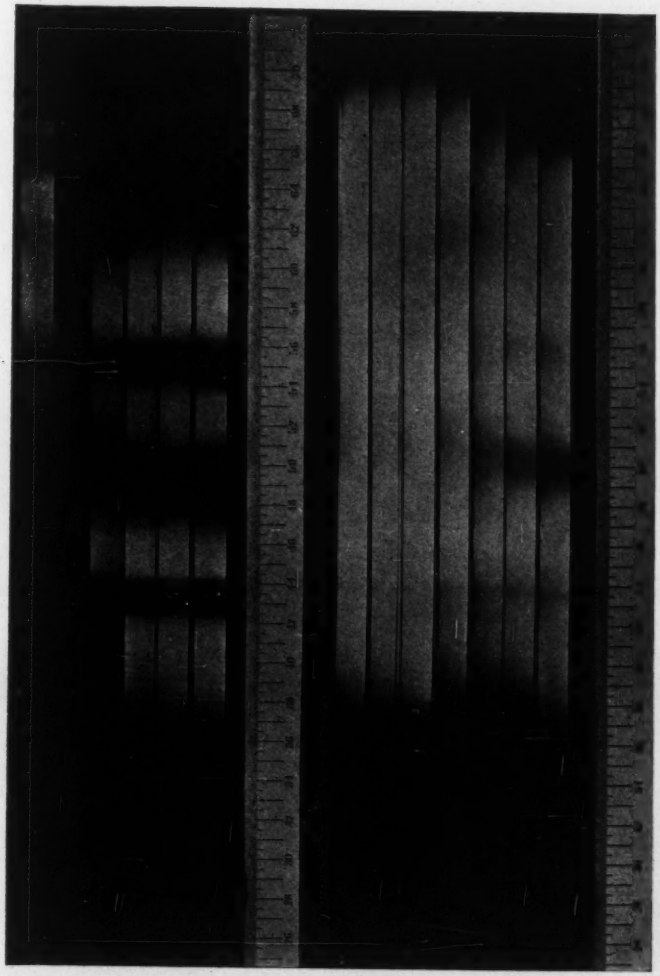
For strip 1 the absorption consists largely of the bands *a*, λ 5000 (very broad and probably double); *b*, λ 4840; *c*, λ 4680; *d*, λ 4530, λ 4440 (latter component very strong); *e*, λ 4310; *f*, λ 4170; and g, λ 4050.

The addition of water causes the absorption in the region λ 6250 to increase. There are also broad absorption bands at λ 5000 and λ 5250, which are very diffuse and are somewhat stronger for the aqueous solution. The *b* glycerol band disappears entirely. The *c* glycerol band breaks up into two, and as the amount of water increases one of these moves rapidly towards the violet. The stronger component remains practically stationary. In strip 7 their wave lengths are λ 4565 (weak) and 4690 (strong and about 30 Angström units wide). The faint component of *d* disappears and there is left a very diffuse band at about λ 4420. The *e* band is double with components at λ 4250 and λ 4290. About these components there is a very considerable amount of general absorption. The *f* band is at λ 4150.

Uranous Chloride in Mixtures of Glycerol and Methyl Alcohol, Glycerol and Ethyl Alcohol, and Glycerol and Acetone.

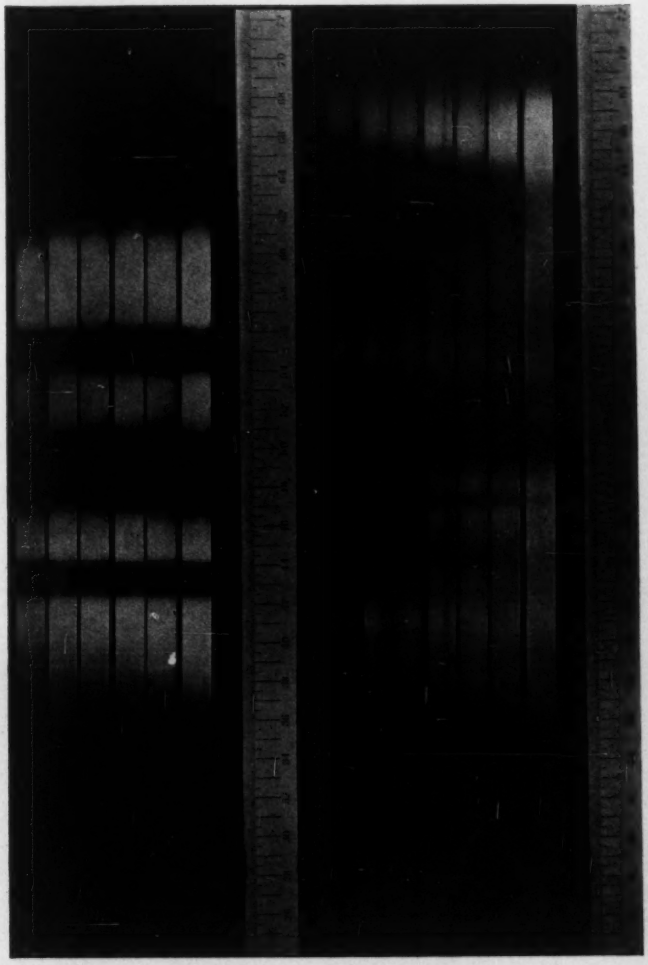
The addition of methyl and ethyl alcohols causes very little change in the bands. Any large addition of acetone causes a precipitate to be formed.

Plate XVIII.



A B

Plate XIX.



A B

	Glycerol solution.	Methyl alcohol.	Ethyl alcohol.	Acetone.
a	5000	5000 (broad)	5000	5000 (weak)
b	4840	4815	4820	4840
c	4680	4650	4660	4680
d	4530 4440	4450 (very broad)	4460	4530 4450 weak
e	4310	4280	4280	4310
f	4170	4140	4140	4180
g	4050	4030	4030	4055

Uranous Chloride in Acetone, in Methyl Alcohol, and in Glycerol.

Plate XXII, *A*, represents the absorption spectra of a solution of uranous chloride in acetone, the depths of cell being 1.2, 2, 3, 5, 8 and 11.5 mm. The slit was 0.10 mm. in width, current in Nernst glower 0.94 ampere, exposure 1.5 minutes to glower and 3 minutes to the spark. The bands are faint and diffuse. By the addition of hydrochloric acid they are made very much stronger, although the wave length is not changed.

Plate XXII, *B*, represents the absorption spectra of uranous chloride in methyl alcohol, the depths of cell being 2, 4, 6, 8 and 12 mm. These solutions were made about six months before being used. Bands appear at λ 6650, λ 6200, λ 5600, λ 5250, λ 4900 to λ 5070, λ 4780, λ 4665, λ 4600, λ 4230, and λ 4110. The absorption is very strong throughout the region λ 4200, and is so general that there is hardly any banded appearance.

Plate XXII, *C*, represents the absorption of a solution of uranous chloride in glycerol containing strontium chloride. The depths of cell were 2, 4, 6, 8, 12 and 24 mm. The absorption spectra show the uranyl bands and the large uranyl blue-violet band. Besides these there is a diffuse band at λ 5300 and a band at λ 6200, which broadens rapidly as the depth of cell is increased. The uranyl bands are located as follows: *a*, λ 4980; *b*, λ 4840; *c*, λ 4680; *d*, λ 4445 (weak band at λ 4530); *e*, λ 4300, to *f*, λ 4170.

Uranous Chloride in Methyl Alcohol and Ether.

Two photographs were made, one of uranous chloride in methyl alcohol (next to the spark spectrum), and one of

uranous chloride in a mixture of about 60 per cent. methyl alcohol and 40 per cent. ether. Further addition of ether caused a precipitate to be formed so that the absorption spectra could not be obtained.

The methyl alcohol solution showed complete ultraviolet absorption to λ 3700. The region λ 4300 showed considerable general absorption due to the blue-violet band. The following uranyl bands appear: *i*, at λ 3880; *h*, at λ 4000; g, composed of two bands, one at λ 4110 and a narrow band about 10 Angström units wide at λ 4135; *f*, two bands, λ 4240 and λ 4285, the latter being quite narrow; *d* and *e*, one very broad band at about λ 4400; *c*, at λ 4610; and *b* at λ 4780. Two bands, λ 4930 (*a*) and λ 5050 are almost merged into each other.

The addition of ether caused the absorption to increase, the ultraviolet absorption extending to λ 3800 and the absorption from λ 4100 to λ 4450 being almost complete. The uranyl bands are slightly shifted towards the red. Their general character remains the same. The wave lengths are approximately: *i*, λ 3890; *h*, λ 4010; *g*, λ 4140; *f*, λ 4260; *de*, λ 4440; *c*, λ 4630; *b*, λ 4790; *a*, λ 4960, and a band at about λ 5050.

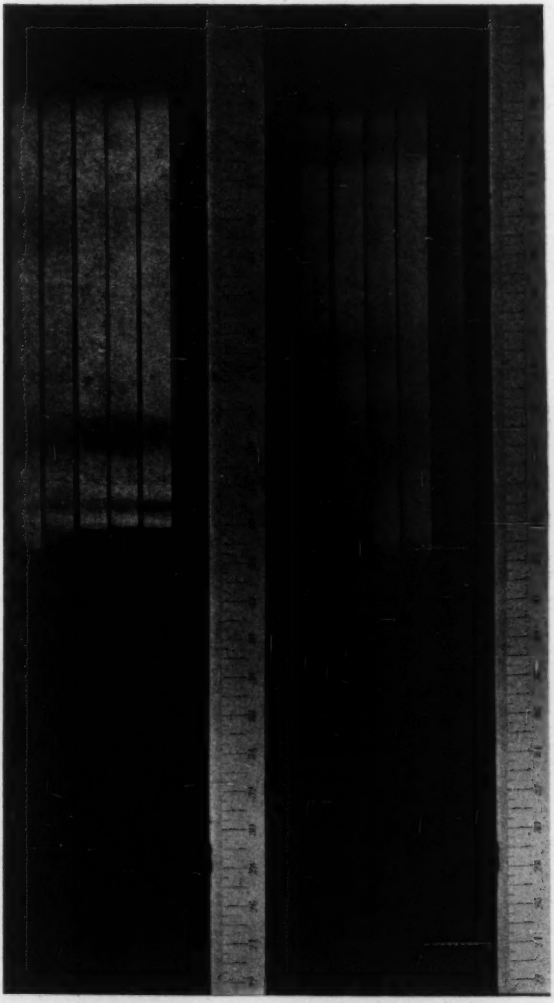
The effect of ether is to cause the bands to shift slightly to the red and to increase the amount of absorption.

Effect of the Presence of Acids on the Uranous Bands.

A spectrogram was made of a 3 mm. solution of 0.17 normal uranous chloride in water (strip 1). To this was added very strong hydrochloric acid until the depth of cell was 6 mm. (strip 2), and finally until it was 12.5 mm. (strip 3), and 24 mm. (strip 4).

The effect of hydrochloric acid is very marked. In general it shifts the uranyl and uranous bands to the red. It causes the uranyl bands to appear much stronger. In an aqueous solution the λ 6400 band is very broad, and the λ 6655 band comparatively narrow. Hydrochloric acid reverses the appearance of these two bands, shifting both towards the red at the same time. The following wave lengths give the effect of hydrochloric acid:

Plate XX.



A B

Plate XXI.

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	Strip 1.	Strip 2.		Strip 1.	Strip 2.
b	....	4800	*b*	4875	5000
c	....	4640	*c*	5520	5620
d	....	4490 (weak)	*d*	6340 (weak)	....
e	4380 (weak)	4420 (strong)	*e*	6430–6600	6500–6570
f	4280 (strong)	4280 (strong)	*f*	6755	6700–6850
g	4130	4150	*g*		

An aqueous solution of uranous chloride in concentrated hydrochloric acid gave the uranyl bands very distinctly. The uranium salt was reduced in this case in the presence of hydrochloric acid. The spectrum is almost identical with that of uranous chloride when hydrochloric acid is added after the reduction has taken place.

The addition of about 20 per cent. strong sulphuric acid to an aqueous solution of uranous and aluminium chlorides has a very marked effect upon the bands. The general effect is to shift the bands towards the violet. For the uranous chloride solution containing aluminium there is a band about 50 Angström units wide at λ 6770 and a band from λ 6460 to λ 6640. These are the water bands. When sulphuric acid is added there is a wide band from λ 6600 to λ 6760, a narrow band at λ 6480, and a wide band running from λ 6200 to λ 6400. Sulphuric acid reverses the breadth of the two red water bands.

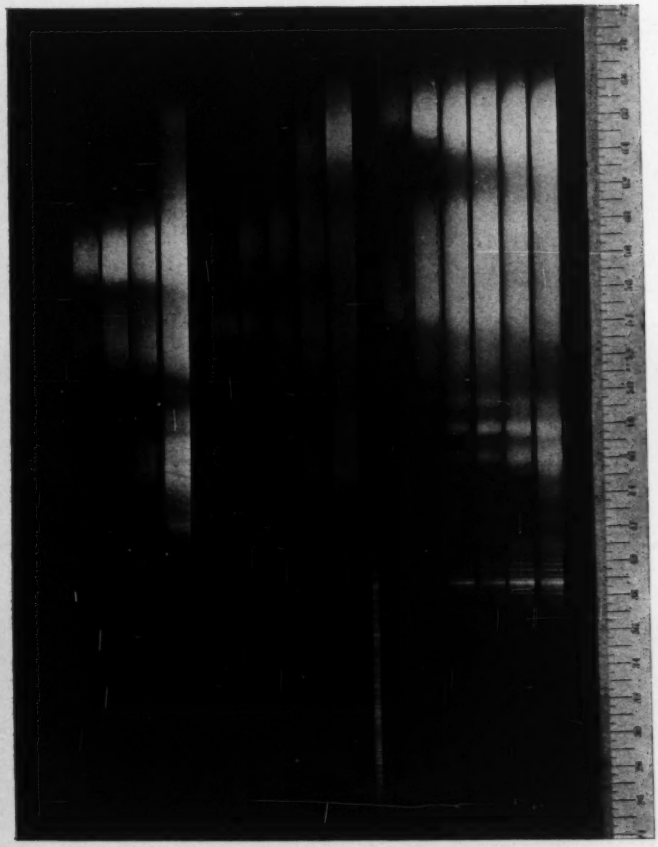
The water band at λ 5500 is shifted to the violet and doubled by the addition of sulphuric acid, the resulting bands being λ 5500 (strong) and λ 5400. The uranyl bands are all shifted to the violet as follows: *a*, λ 4990 to λ 4890; *b*, λ 4780 to λ 4750; *c*, λ 4620 to λ 4560; *d*, λ 4400 (λ 4490 weak) to λ 4360; *e*, λ 4280 to λ 4220; *f*, λ 4140 to λ 4080.

Uranous Chloride in Water and Methyl Alcohol; Water and Acetic Acid; Water and Nitric Acid; and in Water and Sulphuric Acid.

Strip 1, Plate XXIV, *B*, represents the absorption of a 4 mm. layer of a 0.17 normal aqueous solution of uranous chloride; strip 2, that of a solution whose depth has been increased to 6.3 mm. by adding methyl alcohol; strip 3, methyl alcohol added until the depth of layer is 7.5 mm.; strip 4, a 4

	Strip 1.	Methyl alcohol. Strip 3.	Acetic acid. Strip 5.	Nitric acid. Strip 6.	Sulphuric acid. Strip 7.
b	....	....	4785	....	4750 (very diffuse)
c	....	....	4620	....	4550 (very diffuse)
d	....	....	4450	....	4400
e	4380	....	4280–4245	4330 e?	4340
f	4280	4255	4130 *f*?	4240 *f*?	4220 (double narrow component on violet side)
g	4130	....	....	4120 *g*?	4100
	4875	4670 (characteristic)	....	4800 (very diffuse)	4900 (wide and strong)
	5520	5000 (very diffuse)	4900–5000	5450 (very diffuse)	5390–5490 (almost join)
	6340	5250 (very diffuse) 6200 (very diffuse)	5500 (very diffuse)	6500 (50 A. U. wide)	6250–6380
			....	6670–6760	6490 (30 A. U. wide)
	6420–6620 6755	....	6450–6800	...	6610–6760 (quite well-defined)

Plate XXII.



A B C

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mm. layer of 0.17 normal aqueous solution of uranous chloride; strip 5 is the same as 4 to which acetic acid has been added to make the depth of layer 28 mm.; strip 6, a 4 mm. layer of 0.17 normal aqueous solution of uranous chloride, plus 2 mm. of strong nitric acid; strip 7, a 4 mm. layer of 0.17 normal aqueous solution of uranous chloride to which 19 mm. of sulphuric acid had been added.

Uranous Chloride to which Acetic Acid is Added.

Plate XXI, *B*, represents a slightly acid solution of uranous chloride in water to which is added glacial acetic acid until there is five times as much glacial acetic acid present as there was of the original solution. The addition of acetic acid causes a marked change in the absorption. The band *a*, λ 4980, doubles into the bands λ 5020 and λ 4930; *b* and *c* double without being changed very markedly; *d*, λ 4400, is slightly shifted to λ 4420; *e*, λ 4280 to λ 4300; *f*, λ 4140 to λ 4160; and g, λ 4010 to λ 4030; λ 5560 is shifted to λ 5590; λ 6450 to λ 6650 to λ 6500; and instead of the band at λ 6770 there are two bands λ 6650 and λ 6800.

Uranous Bromide.

Plate XIX, *A*, represents the absorption of an 0.8 mm. depth of 0.5 normal uranous bromide in water to which more and more water has been added. The depths of cell are 0.8, 2.8, 12.5, 22, and 35 mm.

The ultraviolet absorption is but slightly changed by the addition of water. The other uranous bands are narrower the greater the dilution of the uranous bromide. For the upper strip the positions of the bands are λ 4280, λ 4370 (these bands form practically a single band), λ 4850 (very diffuse), λ 4970 (these bands merge into each other), λ 5400 to λ 5600, λ 6200 to λ 6650 and λ 6750.

Uranyl and Uranous Acetates.

The action of free acetic acid upon the uranyl absorption bands of an aqueous solution of uranyl acetate is quite small. The bands are made quite narrow and weak. One spectrum gave *b*, λ 4730; *c*, λ 4610; *d*, λ 4470; *e*, λ 4330; and *f*, λ 4210.

This is very similar to the absorption spectra of the anhydrous salt. Uranous acetate in water (Plate XXIII, *B*) gives a lot of weak diffuse bands. The bands are located at *c*, λ 4600; *d*, λ 4460; *e*, 4330; *f*, λ 4200; and *g*, λ 4090. Besides these there are broad bands at $\lambda\lambda$ 5050, 5600, 6700, and 6850.

Absorption Spectrum of Dry Uranous Acetate.

The green precipitate that is formed when a solution of uranous acetate in methyl alcohol stands for several hours was illuminated by light from the Nernst glower, the illuminated salt being over the slit of the spectroscope. The green salt changed to a dark color, probably due to oxidation.

The absorption spectra showed weak diffuse bands at $\lambda\lambda$ 4240, 4350, 4500, 4650, and a wide band running from λ 4900 to λ 5200. If these bands are to be identified as the *f* (λ 4240), *e* (λ 4350), *d* (λ 4500) and the *c* (λ 4650) bands, and their relative intensities are about the same as that of the bands of uranous acetate in methyl alcohol, then the bands are slightly shifted towards the red, this shift being about 50 Angström units.

Uranous Acetate in Methyl Alcohol and Acetic Acid.

To a solution of uranyl acetate in methyl alcohol was added glacial acetic acid and some metallic zinc. The solution becomes green in color after standing a few minutes. In an hour or more a greenish precipitate is formed, and after standing several hours the solution shows only the uranyl bands. The plate represents the absorption spectra of the green uranous acetate. The only variation here is the depth of cell. For the three strips nearest the top the depth of cell was the same.

Starting in the ultraviolet the spectrogram shows a general absorption which extends into the blue for the greater depth of layer. No indication of the blue-violet uranyl band is to be noticed. Several fine bands appear in the blue-violet region. As these coincide very closely in position with the uranyl acetate bands they will be so considered. Of these the *a*, *b*, *c*, *d*, *e*, *f*, and *g* bands appear. The *g* band (λ 4070) is very faint. The *f* band (λ 4200) is stronger and is about

Plate XXIII.

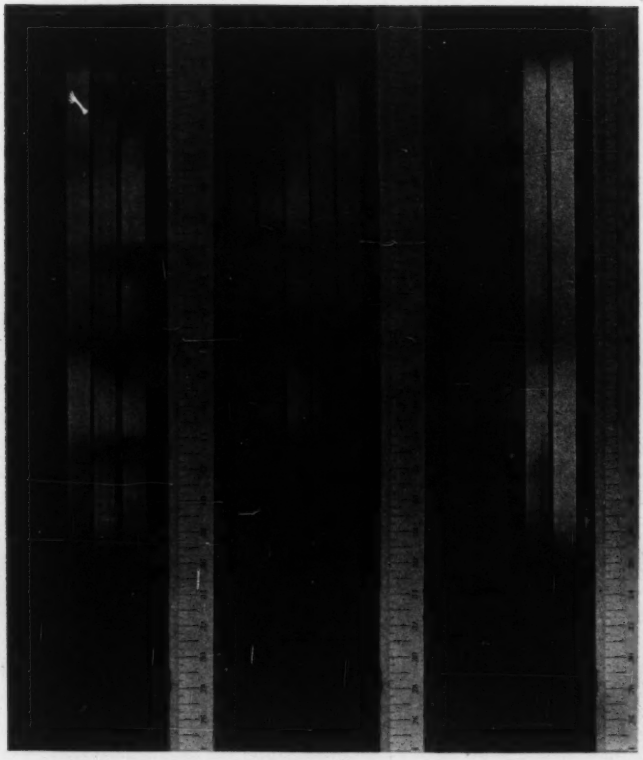

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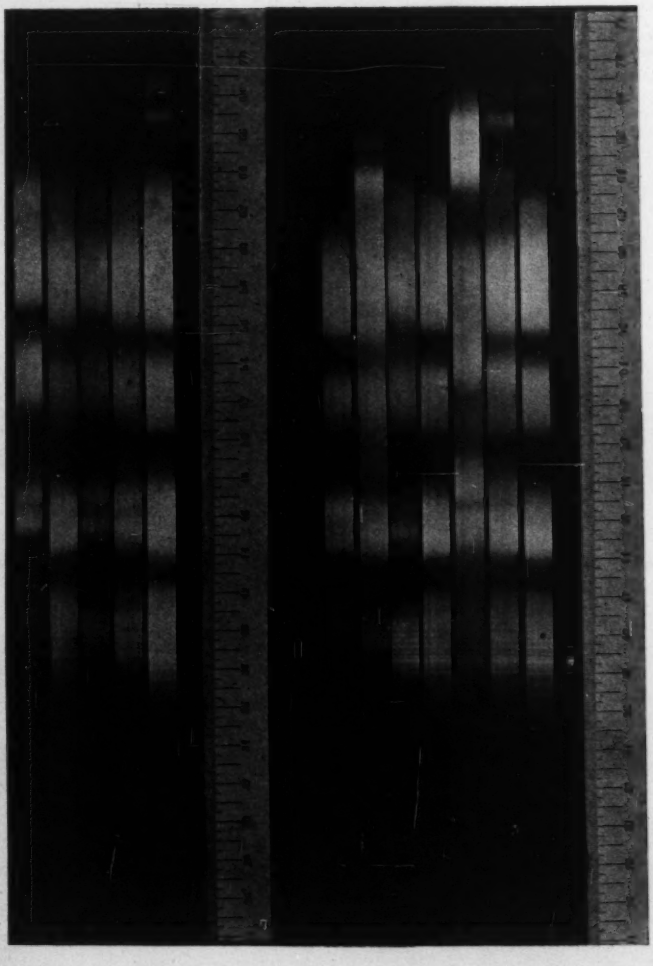
Plate XXIV.



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30 Angström units wide. The *c*, *d*, *e*, and *f* bands appear quite strong, the *e* band being the strongest. It appears to be complex, being composed of a fuzzy band at λ 4285 about 10 Angström units wide; a fine sharp band at λ 4310 about 3 Angström units wide, and a band extending roughly from $\{^{\lambda\ 4315}_{\lambda\ 4316}\}$ to λ 4340. The *d* and *c* bands ($\lambda\lambda$ 4470 and 4610) are about 30 Angström units wide and of about equal intensity. The *a* and *b* bands are very weak ($\lambda\lambda$ 4910, 4740) and appear only on the original negative.

The *a* band with two other very diffuse bands $\lambda\lambda$ 5000, 5100 forms the wide absorption band in this region and the three practically merge into each other. A similar band extends from λ 5550 to λ 5650. In the red there are quite a number of fine bands very similar to the uranyl group in the blue and violet. These are very faint; the widest and strongest appears at λ 6450, this band being about 40 Angström units wide. The other bands are about 20 Angström units wide and are located approximately at $\lambda\lambda$ 6600, 6700, 6800, 6870, and 6920.

Uranous Acetate in Glycerol.

Uranous acetate was obtained as already described. Some of the solution in methyl alcohol and acetic acid was mixed with glycerol and warmed so as to drive off as much alcohol and acid as possible. The solution was filtered hot. The precipitate was green, the filtrate yellow, indicating that the uranium in the glycerol was mostly in the uranyl condition.

The absorption spectra showed several of the uranyl bands. These bands are not nearly so intense as the bands of uranous acetate in methyl alcohol and acetic acid. The *f* band λ 4220 appears to be double. The *e* band consists of a band about 15 Angström units wide at λ 4295, a band at λ 4340, and one at λ 4390; the *d* band, of two bands λ 4480 and λ 4530; and the *c* band, of λ 4630 and λ 4680, the latter being the weaker of the two bands.

The Wave Lengths of the Uranous and Uranyl Bands under Varying Conditions in Aqueous Solutions.

	Uranyl nitrate.	Uranyl chloride.	Uranous bromide.	Uranyl nitrate in HNO_3.	Uranous chloride.	Uranyl acetate.	Uranous acetate.	Uranyl bromide.	Uranyl acetate.	Uranyl sulphate.
a	4870	4920	{4970 / 4880}	4850	4980	4910	....	4880	4910	4900
b	4705	4740	4740	4670	4790 W	4740	....	4720	4740	4740
c	4550	4560	4600	4520	4550 W	4600	4600	4560	4595	4580
d	....	4460	....	4380	4420 W	4460	4460	4450	4455	4460
e	4310	4315	....	4240	{4305 / 4270}	4310	4330	4280	4310	4330
f	4155	4170	....	4140	4150	4160	4200	4160	4160	4200
g	4030	4025	....	4050	4020	4070	4090	....	4070	4070
h	3905	....	....	3920	3910	3970	....	....	3970	3970
i	3815	....	....	3810	....	3830	....	....	3830	3850
j	3710	....	....	3750	....	....	....	....	....	3740
k	3605	....	....	3670	....	....	....	....	....	3630
l	3515	....	....	3590	....	....	....	....	....	3530
m			6740	3520	5500	....	5050			
			6480	....	6500	....	5600			
			5500	....	6750	....	6700			
					6340	....	6850			

Alcoholic Solutions of Uranium Salts.

Uranous chloride in methyl alcohol gives bands at $\lambda\lambda$ 6650, 6250, 5600, 5260, 4900–5070, 4780, 4665, 4600, 4230, 4410.

Uranous bromide in methyl alcohol gives bands at $\lambda\lambda$ 6650, 6200, 5650–5500, 5250, 4950–5100, 4680S, 4450–4300, 4150.

	Uranous chloride in methyl alcohol.	Uranyl nitrate in methyl alcohol.	Uranous acetate in methyl alcohol.	Uranyl nitrate in ethyl alcohol.	Uranous chloride in ethyl alcohol.	Uranyl acetate in methyl alcohol.	Uranous bromide in methyl alcohol.	Uranyl chloride in methyl alcohol.	Uranous chloride in methyl alcohol.	Uranyl chloride in ethyl alcohol.	Uranous chloride in ethyl alcohol.
	5050	....	....	5000	5050 to	4880	5070	....	....	....	....
a	4930	4930	4910W	....	4950	4900	4900	4930	5000	4900	5000
b	4780	4760	4740W	4800	4710	4720	4780	4760	4815	4750	4820
c	4610	4610	4610	4630	....	4590	4665	4610	4650*b*	4580	4665
d	4400*b*[1]	4455	4470	4475	....	4450	....	4465	4450	4400	4460
e											
f	4285	4325	4330	4325	....	4320	....	4345	....	....	....
g	4135	4190	4310	4180	4290 W	4190	4230	4220	4280	4250	4280
	4110		4285								
h	4000	4070	4200	4080	....	4070	4110	4090	4140	4100	4140
i	....	3965	4070	3970	....	3980	....	3980	4030	3980	4030
j	....	3855	....	3875	....	....	....	3860		3860	....
								3760	....		
	5260	....	....	....	5280						
	6250	....	....	....	6250						

[1] *b* is broad.

Glycerol Solutions.

	Uranous acetate in glycerol.	Uranous bromide in glycerol.	Uranyl chloride in glycerol.	Uranyl chloride in glycerol.	Uranyl nitrate in glycerol.	Uranous sulphate in glycerol.	Uranous chloride in glycerol.	Uranous chloride in glycerol.
a	....	....	5060 w	5050	5040 5020	....	....	....
b	4680 4630 w[1]	....	4980 w 4840 s 80[2]	4900	4910 4750	$4780 + H_2SO_4$	5000 4790	5000 4840
c	4530 4480	4700?	4680 s 80	4720	....	4640	....	4680
d	4390 4340 4295	4550 w? 4430 w	4530 n.d.[3] 4440 w	4540 4400	....	4480	4550 4420	4530 w 4450
e	4220	....	4300	4260	4350	4365	4300	4310
f	....	4200?	4170	4140	4220	4250	4170	4260 w 10
g	....	....	4050 w	4025	4100	4120	4050	4170
h	....	....	3930 w	3920	3970	4010	....	....
i	....	....	3800 w	....	....	3900	....	....
j	....	....	....	....	....	....	....	....
k	....	....	....	....	....	3750	....	....
l	....	....	....	....	....	3650	....	....

[1] w means weak.
[2] s = strong, 80 = A. U.
[3] n. d. = narrow and diffuse.

Uranyl Salts in the Presence of Free Acid.

	Uranous chloride in water.	Uranous chloride with hydrochloric acid.	Uranyl acetate in acetone with acetic acid.	Uranyl acetate in water.	Uranyl acetate with acetic acid.	Uranous acetate in water.
a	4980	5000	....	4910	....	....
b	4790	4800	4620?	4740	4730	....
c	4550	4630	4460?	4595	4610	4600
d	4420	4430	4330?	4455	4470	4460
e	{4305 / 4270}	4270	4220?	4310	4330	4330
f	4150	4140	....	4160	4210	4200
g	4020	4020	....	4070	....	4030
h	3910	....	....	3970	....	....
				3830		
	6770					
	6550					
	5620					

Effect of the Presence of Foreign Salts.

	Uranyl chloride in water.	Uranyl chloride + $AlCl_3$.	Uranyl chloride + $ZnCl_2$.	Uranous chloride + $AlCl_3$.	Uranous chloride + H_2SO_4.
a	4920	4950	4930	4990	4890
b	4740	4790	4770	4780	4750
c	4560	4620	4600	4620	4560
d	4460	4480 to 4420	4400	{4490 / 4400}	4360
e	4315		4245	4280	4220
f	4170	4270	4115	4140	4080
g	4030	4135	....	....	....
h	....	4010	....	....	....
i	....	....	....	....	....

Effect of Free Acid.

	Uranyl nitrate in water	Uranyl nitrate to which H_2SO_4 is added.	Uranyl sulphate in water.	Dry uranyl nitrate in HNO_3.	Uranyl sulphate in H_2SO_4.	$UO_2(NO_3)_2 \cdot 6H_2O$ in HNO_3.	Uranyl chloride in water.	Uranyl chloride + $\frac{1}{2}$ HCl.
a	4870	4925	4900	4850	4930	4790	4920	4950
b	4705	4750	4740	4670	4750	4670	4740	4800
c	4550	4560[1]	4580[1]	4520	4560[1]	4510	4560	4635
d	....	4380	4460	4380	4380	4370	4460	4480
e	4310	4240	4330	4240	4240	4230	4315	4420
f	4155	4100	4200	4140	4100	4125	4170	4280
g	4030	....	4070	4050	....	4000	4025	4050
h	3905	3980	3970	3920	3980	3900	....	4015
i	3815	3870	3850	3810	3870	3790		
j	3710	3770	3740	3750	3770	3670		
k	3605	3660	3630	3670	3660	3570		
l	3515	3560	3530	3590	3560			
				3520				

[1] Double.

Any small differences in the wave lengths of the absorption bands of uranous solutions under different conditions are probably due to the presence of varying amounts of zinc used in reducing the uranyl to the uranous condition.

General Discussion of Results.

Previous investigators have in many instances spoken of the absorption of light by molecules, ions, or aggregates of these. At present, however, spectroscopists are more and more inclined to consider the negative electron as the chief absorber of light in the visible and ultraviolet portions of the spectrum. Whether the absorbing electron is the same as the electron found in vacuum discharge tubes, or emitted by radioactive elements, is at present a very much discussed subject. It seems to be quite certain that the masses of many of the absorbers are not of molecular magnitude. It is equally certain, as experiments show and as theory indicates, that the various coefficients which define the equations of motion of the absorber are *functions of the conditions under which the absorbers exist.* If the absorbers are electrons we may think of them as being within or in close proximity to the atom. Such absorbers would be expected to have their period, coefficient of damping and other coefficients, greatly modified by the formation of aggregates, solvates, *etc.*, and such seems to be the case. According to the present theory of the conductivity of solutions it would be expected that if the absorbers existed in or about the atom, their properties would be very greatly affected by the given atom existing in an ionic condition or as part of a molecule. Consequently, at great dilutions, it would be expected that the absorption of a colored solution of a salt would be entirely independent of the salt when the anion was the carrier of the absorbers. In the absorption spectra of solutions there are but few examples where the absorption spectra of different salts with the same cation are very different from each other. There is one important exception in the case of aqueous solutions of the uranyl salts. The uranyl nitrate bands are all of shorter wave lengths than the bands of the other uranyl

salts. The absorption spectra of these salts have been photographed by us over quite wide ranges in concentration, and no evidence has been obtained that indicates any dependence of the wave lengths of the uranyl bands on the concentration.

Although more and more spectroscopic phenomena are being explained by means of the electron theory, yet there is a general tendency to consider that only the electrons in a few atoms are in a condition to absorb or emit light at any moment. The nature of these conditions is at present not well known, but it seems probable that they are *exceptional states*, in some cases at least. For instance, only a few of the sodium atoms take part in the absorption of the *D* lines at any particular time, and the same is probably true of neodymium and erbium salts in solution or in the solid state. It is supposed by some physicists that absorption or emission may take place during ionization, as, for example, when an electron leaves or returns to an ion. Upon a basis such as this are laid the theories of dynamic isomerism, isorepesis, and Stark's theory of the spectrum of canal rays and of fluorescence. On such a theory as this it may be supposed that in solutions the absorption takes place in those molecules that are undergoing dissociation, or in those ions that are combining to form molecules. In the case of the uranyl nitrate bands the combined action of water and the NO_3 group has a hypsochromous effect upon the wave lengths of these bands. That it is due to the combined action of the water and the NO_3 group is shown by the fact that in other solvents the NO_3 group does not have this hypsochromous effect; while in water it is only the nitrate bands that have the smaller wave lengths. According to the theory of dynamic ionization, the absorption of light could take place while the NO_3 groups were near the UO_2 group, so that the periodicity of the absorbed light would be affected. According to this theory, however, the number of ionizations through which a molecule would pass would probably be a function of the concentration; and thus the intensity of the absorption bands should be a function of the concentration. But for uranyl nitrate Beer's law holds at least approximately, whereas con-

siderable variations would be expected from the above theory. If the absorption takes place during periods of ionization, and the intensity of the absorption depends only on the number of these ionizations, then the fact that Beer's law holds shows that the number of these ionization phenomena is independent of the concentration. The fact that the absorption spectrum of uranyl nitrate crystals is very similar to that of solutions indicates that the uranyl groups that take part in absorption are about as closely united with water and the NO_3 group in solution as they are in the solid.

It may, however, be said in general *that the anions of the various colored salts*—and in practically all cases it is the anion that exhibits banded absorption—*play a much less important rôle in modifying the spectra than the solvent.* Different salts of the same anion in the same solvent usually have the same absorption spectra. On the other hand, the absorption spectra of the powdered salts themselves may be very different. This fact shows that the *solvent plays a most important part in the absorption* and it *seems highly probable that in a large number of cases there is an "atmosphere" of the solvent molecules about the colored absorber. In a word, there is solvation.* However, in the case of the nitric oxide[1] spectrum it seems possible to have the gas existing in solution and at the same time having its absorption spectra unaffected. The nitric oxide spectrum occurs only under very special conditions, and has not thus far been obtained for solutions of the gas, but only when some acid is added to nitric acid or a nitrate.

Whereas the absorption of different salts of the same colored anion is in general very similar, on the other hand *the absorption spectra of the same salt in different solvents are often very different indeed.* Formerly this effect of the solvent was thought to be due to a difference in the value of the dielectric constant, but Jones and Anderson have pointed out that the most probable cause is the *formation of solvates, or more or less stable compounds of the salt and solvent.* The reason *for this conclusion is that in mixtures of two solvents, each set of*

[1] Physic. Rev., **30**, 279 (1910).

solvent bands appears, the intensity of any solvent band being a function of the relative amounts of the solvents present. That these compounds or solvates have a definite composition seems to be indicated by the fact that for most of the neodymium, uranyl, and uranous salts there appears only a single set of "solvent" bands for each solvent; and in mixtures of these solvents in most cases but two sets of bands are necessary to explain the results. The persistence of solvent bands varies quite widely for the different solvents, and appears to be greatest for water and glycerol and less for the alcohols. The persistence of any one solvent band seems to be the same for quite widely different salts. There are, however, some cases where it may be possible that intermediate solvates are formed. The spectrum of neodymium chloride dissolved in mixtures of water and glycerol seems to indicate that the "water" band λ 4274 gradually shifts to the "glycerol" bands.

Probably no salts show more characteristic bands than some of the uranous salts in the various solvents: water, the alcohols, acetone, and *glycerol.* It seems probable that the absorbers are the same for the corresponding bands of any two "solvent" spectra. An important fact indicating this is given by Becquerel, who found the Zeeman effect to be the same when different solvents of the same salt were used. It is generally conceded that at higher temperatures solvates are broken up. At present, work is being done on solutions containing mixtures of two solvents in such proportion as to give both sets of solvent bands. As the critical temperature of one solvent is approached, according to the foregoing theory the bands of that particular solvent should disappear. In many cases the two sets of solvent bands differ not only in wave lengths but also in intensity and in the number of components. Of all the bands of the neodymium absorption spectra, the "water" band λ 4274 is one of the strongest and one that is freest from neighboring bands. Yet, in different solvents this band may become a doublet, a triplet, or may even apparently break up into a whole series of bands. It is quite certain that when the mechanism of these changes is known, our knowledge of chemical compounds will be increased very

greatly, and it is very important that gradual changes of solvent or salt may be made at low temperatures where the bands are much sharper, and work is now in progress on this problem.

In some cases it is possible to break up the absorption bands by chemical methods into very fine bands. A very striking example is the case of uranyl and uranous salts in acetone solutions. The uranyl salt in acetone gives six bands in the region λ 5000 that are characteristic of acetone solutions. By the addition of hydrochloric acid to an acetone solution the uranyl bands are broken into fine components. Several of the uranyl bands become triplets and some doublets. But the most marked example is the addition of hydrochloric acid to an acetone solution of uranous chloride. Several very broad uranous bands are broken up into a number of very fine and quite intense bands.

One very interesting result has come to light from the examination of the effect of free nitric acid on the absorption spectra of uranyl nitrate; of sulphuric acid on the sulphate; acetic acid on the acetate; or hydrochloric acid, calcium or aluminium chloride on the chloride. In general, the *presence of these foreign reagents causes the uranyl bands to become more intense and, in most cases, narrower. The action of all the above reagents except nitric acid is to cause the uranyl bands to be shifted towards the red.* Nitric acid, however, causes large shifts towards the violet. The above reagents have a similar effect on the corresponding uranous bands.

The explanation of the above effects seems possible by supposing that aggregates are formed. In the case of neodymium salts the effect of the above reagents is very small, and nitric acid, instead of causing the neodymium nitrate bands to become narrower, stronger, and to be shifted towards the violet, simply causes the bands to become much more diffuse. The other reagents cause the neodymium bands to become diffuse, weaker, and to broaden somewhat towards the red.

In addition to trying the effect of acids upon uranium salts of the same acid, *spectrum photographs were made of the effect produced by adding acids to different uranyl, uranous,* and

neodymium salts. Uranyl nitrate was treated with sulphuric, hydrochloric, and acetic acids; uranyl and uranous acetates with various acids; various uranous salts and neodymium acetate with nitric acid. These salts and acids were selected, since they showed the greatest spectroscopic changes. Especially interesting are the spectrograms of uranous salts treated with nitric acid.

The spectrophotographs of chemical reactions show, invariably, that the changes produced in the spectra as one salt is transformed into another are gradual, whereas in changing the solvent this is not the case. *For instance, when uranyl nitrate is transformed into uranyl sulphate, the uranyl nitrate bands gradually shift into the sulphate position.* The same effect is produced when solutions are made containing different amounts of uranyl nitrate and uranyl sulphate. Further addition of sulphuric acid causes the bands to shift still more. An example is given where to a small amount of a solution of uranyl nitrate in nitric acid a large amount of sulphuric acid is added.

	Nitrate in nitric acid.	Same plus sulphuric acid.		Nitrate in nitric acid.	Same plus sulphuric acid.
a	4850	4930	*h*	3920	3980
b	4670	4750	*i*	3810	3870
c	4520[1]	4560[2]	*j*	3750	3770
d	4380	4380	*k*	3670	3660
e	4240	4240	*l*	3590	3560
f	4140	4100			
g	4050				

It will be seen that the shifts in these cases are quite large, and the moving together of the *f* and *g* bands is especially remarkable. The chemical changes studied thus far spectroscopically have been, in most cases, confined to aqueous solutions. Changes effected in other solvents are usually smaller. For instance, the addition of sulphuric acid to a glycerol solution of uranous sulphate simply causes the *g*, *h*, and *i* bands to be shifted about 20 Angström units to the violet. Similar changes are often produced by adding salts containing the cation of the acid. For instance, it has been found

[1] Narrow.
[2] Double.

that the absorption spectra of uranyl chloride in a concentrated aqueous solution of aluminium chloride, or zinc chloride, or hydrochloric acid, are very similar to those of uranyl and calcium chlorides in methyl alcohol, or of uranyl chloride in ethyl alcohol.

When nitric acid is added to an aqueous solution of uranous acetate, it is found that the oxidation of the uranous salt does not occur when small amounts of acid are added, but that in this case the uranous bands are shifted to the violet. The uranyl bands pass through several stages and change very greatly, indicating that the chemical reaction is quite complex.

The absorption spectra of uranous salts usually show the uranyl bands, and in some cases these are very strong. The question immediately arises as to whether the uranyl bands are common both to the uranyl and uranous salts. It seems probable that they are characteristic of only the uranyl salts, although this is not certain. Uranous salts have been obtained which show only a strong band appearing in about the same position as that of the blue-violet uranyl band, and this indicates that the presence of uranyl bands is due to the uranyl salt which has not been reduced. In most of the changes of solvent and salt it has been found possible to follow the individual uranyl bands throughout the reactions which took place, and this seems to indicate that the absorption is due to a system of some kind which preserves its entity throughout all these changes.

The gradual shift of the absorption bands as one salt of a metal is transformed into another salt by the addition of more and more free acid is very important.

In the reduction of uranyl salts to uranous salts it is very difficult to produce a complete transformation. As a result, most of the uranous salts show the uranyl bands, and probably on account of the presence of foreign salts or acids these uranyl bases often appear quite strong. In some cases, however, solutions of uranous salts were obtained which did not appear to have any uranyl bands in their absorption spectrum. Recently some spectrophotographs have been made of the

oxidation of uranous into uranyl salts by the addition of small amounts of hydrogen dioxide. These spectrograms seem to indicate clearly that the "uranyl" bands in the region λ 3000 to λ 5000 are characteristic of the uranyl salts only.

Rise in temperature causes the general absorption of any salt in water to increase and also causes the bands to broaden and become more intense.

The increase in the general absorption with rise in temperature is much greater for concentrated solutions. This also holds true for bands of the second type, and to a small extent for bands of the third type.

The presence of calcium and aluminium chlorides causes the chromium chloride bands to widen very unsymmetrically on the long wave-length edge with rise in temperature.

The uranyl chloride bands are shifted towards the red with rise in temperature. No shift for the uranyl nitrate could be detected. Uranyl nitrate, however, dissolved in strong nitric acid showed quite a large shift. The uranyl acetate and sulphate bands were slightly shifted.

No shift with rise in temperature was noticed for solutions of neodymium or erbium salts. When calcium chloride is present the neodymium chloride bands are, however, shifted, and the remarkable fact is observed that the bands then become fainter with rise in temperature. This latter phenomenon is considered to be very important, and it may be that the abnormal Zeeman effect observed by Becquerel is due to the presence of foreign compounds in the tysonite and xenotin crystals.

When a neodymium salt is dissolved in water and alcohol in such a proportion that the "water" and "alcohol" bands are of equal intensity at a given temperature and a given concentration, it is found that these bands do not obey Beer's law.

Change of temperature[1] does not have the same effect upon the "water" and "alcohol" bands of a solution when these appear together.

One of the most important points brought out in this in-

[1] Physik. Z., **11**, 668 (1910).

vestigation is the additional evidence furnished for the existence of solvates in solution, these solvates having very different compositions and very different spectra, depending upon the solvent in which the salt in question was dissolved.

It is not too much to say that by this work the whole solvate theory is placed upon a firmer basis.

This suggests the thought: Of what significance or scientific use is the solvate theory of solution?

Bearing of the Solvate Theory of Solution.

The evidence for the solvate theory of solution which has been furnished in this laboratory as the result of somewhat more than a dozen years of investigation has recently been brought together and briefly discussed.[1] The evidence is so unambiguous and convincing that ions and some molecules combine with more or less of the solvent that it can now be accepted as a fact of science.

This, however, raises a number of questions: What relation does the solvate theory of solution bear to the theory of electrolytic dissociation?

Does the solvate theory help us to explain any of the apparent discrepancies in the theory of electrolytic dissociation? Does the solvate theory help us to explain the facts of chemistry in general and of physical chemistry in particular? Why is the nature of solution so important, not only for chemistry but for science in general?

The Solvate Theory and the Theory of Electrolytic Dissociation.

When Arrhenius proposed the theory of electrolytic dissociation the question was not even raised as to the condition of the ions in the solution except that they behave as if they existed independently of one another in solution. The theory simply said that molecules of acids, bases and salts in the presence of a dissociating solvent like water break down to a greater or less extent into charged parts called ions, the cations or positively charged parts being electrically equivalent to the anions or negatively charged parts. The cations are usually simple metallic atoms carrying one or more unit

[1] Z. physik. Chem., **74**, 325 (1910).

charges of positive electricity. The cation might, however, be more or less complex, as illustrated by ammonium and its substitution products. The anion is usually complex, consisting of a larger or smaller number of atoms. It may, however, be an atom carrying negative electricity as in the case of the halogen acids and their salts.

The degree of dissociation is determined by the nature of the acid, base or salt. Strong acids and bases are greatly dissociated. Indeed, the degree of dissociation determines their strength. Nearly all of the salts are strongly dissociated compounds, there being, however, some exceptions, as, notably, the halogen salts of mercury, cadmium and zinc. There are, however, considerable differences in the amounts to which salts in general are dissociated at the same dilution.

The quantitative evidence furnished by Arrhenius and others for the theory of electrolytic dissociation is so convincing that few chemists of any prominence who have carefully examined the evidence have ever doubted the general validity of the theory, and the theory has become substantiated by such an abundance of subsequently discovered facts that it has now become a law of nature and a fundamental law of chemical science.

Arrhenius saw and pointed out clearly the importance of ions for chemistry, and Ostwald and his pupils have shown that chemistry is essentially a science of the *ion*, molecules for the most part being incapable of reacting chemically with molecules; and Nernst has shown that the ion is the active agent in all forms of primary cells.

The theory of electrolytic dissociation, as already stated, does not raise the question as to the relation between the ion and the solvent. At the time that the theory was proposed chemists did not know and probably had no means of finding out whether the ion is or is not combined with the solvent in contact with it. The solution of this problem remained for subsequent work.

Some of the many lines of evidence that ions and certain molecules are combined with a larger or smaller number of

molecules of the solvent, and in many cases with a very large number of molecules of the solvent, have been recently discussed briefly by Jones in an article in the *Zeitschrift für physikalische Chemie.*[1]

The amount of the solvent combined with an ion is primarily a function of the nature of the ion or ions in the solution. It is, however, conditioned very largely by the dilution of the solution, and also by the temperature.

The evidence, some of which is given in the paper referred to above and the remainder in other publications of the results of investigations carried out in this laboratory during the past dozen years, shows that the power of the ions to combine with the solvent is by no means limited to water and aqueous solutions but is a property of solutions in general. The alcohols, acetone, glycerol,[2] *etc.*, combine with certain substances dissolved in them, and it seems more than probable that all solvents combine with the dissolved substances to a greater or less extent. In a word, we do not have simply a theory of hydration, but a theory of solvation in general, which is an essential part of any generalization which would take into account the facts presented by solution.

The solvate theory of solution has been regarded in some cases as a rival of the electrolytic dissociation theory of solution, if not directly antagonistic to it. Such is not at all the case. The solvate theory begins where the theory of electrolytic dissociation ends. The latter gives us the ions from molecules and the former tells us what is the condition of the ions in the presence of a solvent after they are formed.

The solvate theory of solution, then, simply supplements the theory of electrolytic dissociation, and both must be taken into account if we ever wish to understand the phenomena presented by solution.

Does the Solvate Theory Help to Explain Any of the Apparent Exceptions to the Theory of Electrolytic Dissociation?

Given the theory of solvation in solution together with

[1] "Evidence Obtained in This Laboratory during the Past 12 Years for the Solvate Theory of Solution." Z. physik. Chem., **74**, 325 (1910).

[2] "Conductivity and Viscosity in Mixed Solvents" by H. C. Jones and Coworkers. Carnegie Institution of Washington, Pub. No. 80.

that of electrolytic dissociation, the first question that arises is, does the former really aid us in explaining the phenomena presented by solutions?

Shortly after the theory of electrolytic dissociation was proposed it was recognized and repeatedly pointed out that after all it is only a theory of "ideal solutions," *i. e.*, very dilute solutions. It was shown not to be able to explain many of the phenomena presented by even fairly concentrated solutions. Indeed, it often could not deal quantitatively with the very solutions with which we work in the laboratory.

The explanation of this shortcoming was not fully seen and an analogy was resorted to. It was pointed out that the laws of Boyle and Gay-Lussac for gases hold only for "ideal gases," *i. e.*, dilute gases, but do not hold for gases of any considerable concentration.

It was stated that the gas laws when applied to solutions could not be expected to hold more generally than when applied to gases, and there the matter was allowed to rest.

In the early days of the theory of electrolytic dissociation it was, however, pointed out that we have a fairly satisfactory explanation of why the simple gas laws do not hold for concentrated gases, and this was expressed in the equation of Van der Waals, while no analogous explanation was offered in the case of solutions.

That this point was well taken is obvious to any one. A theory of solution to be of the greatest value must be applicable to all solutions regardless of the nature of the substance, regardless of the nature of the solvent, and regardless of the concentration of the solution.

The explanation of these apparent exceptions to the theory of electrolytic dissociation presented by concentrated solutions has been furnished by the solvate theory. We now know that for solutions in general a part of the solvent is combined with the dissolved substance. While the amount of the solvent combined with any one ion is greater the more dilute the solution, at least up to a certain point, the total amount of the solvent in combination with the dissolved substance is greater the more concentrated the solution.

That the amount of combined solvent may become very great even relatively to the total amount of solvent present can be seen from the following facts: In a normal solution of calcium chloride about two-fifths of the total water present is combined with the dissolved substance. In a three-normal solution of calcium chloride about five-sevenths of the total water is combined.

In the case of a normal solution of aluminium chloride in water about five-eighths of the water present is combined with the dissolved substance, while in a two-normal solution about five-sixths of the water present is in a state of combination.[1]

What we suppose to be a normal solution of calcium chloride is, therefore, more than one and one-half times normal; while what we suppose to be a three-normal solution is in reality more than eight times normal. In the case of aluminium chloride, what we suppose to be a normal solution is more than twice normal, while what we prepare as a twice normal solution is about twelve times normal.

These few facts, taken from thousands of a similar character, show that even fairly concentrated solutions are much more concentrated than we would suppose from the method of their preparation, while very concentrated solutions are many times more concentrated than, without the facts of solvation, we should be led to think.

The general conclusion is that even fairly concentrated solutions are much stronger than if no solvation occurred, and are much more concentrated than we are accustomed to consider from the amount of substance added to a given volume of the solution—more or less of the water present being in combination and only the remainder playing the rôle of solvent. Without the theory of solvation we have hitherto regarded all the water present as acting as solvent.

We should therefore not expect the laws of gases to apply to such solutions when we had no idea what their true concentration was. Now that we know their concentration we

[1] "Hydrates in Aqueous Solution," by H. C. Jones and Coworkers. Carnegie Institution of Washington, Pub. No. 60.

find that the laws of gases are of as general applicability to solutions as to gases, holding not simply for dilute but also for concentrated solutions.

The theory of electrolytic dissociation, supplemented by the theory of solvation, is then not simply a theory of dilute or "ideal" solutions, but a theory of solutions in general.

Does the Solvate Theory Aid Us in Explaining the Facts of Chemistry in General and of Physical Chemistry in Particular?

To answer this question at all fully would lead us far beyond the scope of this paper. A few facts bearing upon this question can, however, be taken up. Take for example the action of the hydrogen ion both in the formation and the saponification of esters. In the presence of the alcohols the hydrogen accelerates greatly the velocity with which an ester is formed; while in the presence of water it causes the ester to break down into the corresponding acid and alcohol.

In terms of ordinary chemical conceptions it is difficult, not to say impossible, to interpret these reactions—the hydrogen ion under one set of conditions undoing what under other conditions it effected.

In terms of the solvation theory these reactions admit of a very simple interpretation. While the hydrogen ion is not strongly solvated, yet work in this laboratory has shown that all ions are more or less solvated. In the presence of alcohol the hydrogen ion therefore combines with a certain amount of this solvent. The hydrogen ion plus the alcohol combined with it unites with the organic acid, forming complex alcoholated ions, which then break down, forming the ester.

On the other hand, the hydrogen ion in the presence of water combines with a certain amount of this solvent. The hydrated hydrogen ion, together with the water united with it, combines with the ester, forming a complex hydrated ion which then breaks down into the corresponding acid and alcohol, setting the hydrogen ion free again.

For a fuller discussion of this reaction see the paper by E. Emmet Reid.[1]

[1] This Journal, **41**, 504 (1909).

A reaction analogous to the above is that of hydrogen ions on amides in the presence of water, on the one hand, and of alcohol on the other. In the presence of water the hydrated hydrogen ion combines with the amide, forming a complex hydrated ion which then breaks down, yielding ammonia and acid, the ammonia, of course, combining with the acid.

In the presence of alcohol the alcoholated hydrogen ion combines with the amide, forming a complex alcoholated ion which then breaks down into ammonia and the ester of the acid in question.

Hydrogen ions in a mixture of water and alcohol, which would contain both hydrated and alcoholated hydrogen ions, give both reactions simultaneously; but as Reid has pointed out, in the presence of an equal number of molecules of water and alcohol, the tendency of the hydrogen ion to hydrate is greater than the tendency to form alcoholates, and under these conditions the first reaction proceeds much more rapidly than the second.[1]

A very large number of types of reactions could be discussed illustrating this same point, *i. e.*, the value of the solvate theory in interpreting chemical reactions.

When we turn to physical chemical processes the solvation of the ions has to be taken into account at every turn. The velocities of the ions are of course a function of the degree of their solvation, and the behavior of the ions, both chemically and physica ly, is a function of their velocities. The effect of dilution, and especially of temperature, on reaction velocities is largely a question of the velocities of the ions present, which, in turn, are a function of the degree of their solvation.

In determining the actual concentration of a solution the amount of the solvent combined with the ions must be taken into account, as has already been pointed out, and without knowing the actual concentrations of solutions quantitative chemistry would be impossible.

The solvate theory has thrown a flood of light on the whole subject of the conductivity of solutions, or the power of the ions to carry the electric current. It has shown us why the

[1] THIS JOURNAL, **41**, 509 (1909).

conductivity of lithium salts is less than that of sodium and potassium, notwithstanding the fact that the lithium ion is much smaller and lighter than the atom of sodium and potassium. We now know that the lithium ion is much more hydrated than the ions of sodium and potassium, and the mass of the moving ion is really much greater than that of sodium or potass um.

When we come to the temperature coefficients of conductivity, the solvate theory has enabled us to interpret results which, without its aid, would be meaningless. We now know why ions with the greater hydrating power have the larger temperature coefficients of conductivity. We know why ions with the same hydrating power have approximately the same temperature coefficients of conductivity, and why dilute solutions have larger temperature coefficients of conductivity than concentrated solutions;[1] and we could multiply examples almost without limit, did space permit, of the effect of the solvate theory on physical chemistry.

Why is the Nature of Solutions of such Vital Importance not only for Chemistry but for Science in General?

The fact is well recognized that modern physical chemistry has reached out into nearly every branch of science and has had an important influence on many of them. The question arises: Why is this the case? The answer is that physical chemistry is primarily a science of solutions.

This answer may not at first sight appear to be self-evident, but a moment's thought will show its general correctness. The whole science of chemistry is primarily a science of solutions in the broad sense of that term. By solutions is meant not simply solutions in liquids as the solvent, but solutions in gases and in solids as well, and not simply solutions at ordinary temperatures but also at elevated temperatures. If we think of chemical reactions in general we will realize what a small percentage of them take place out of solution. Therefore, the nature of solution is absolutely fundamental for chemistry. This applies not simply to general chemistry, including

[1] Jones: THIS JOURNAL, **35**, 445 (1906)

the chemistry of carbon, but also to physiological chemistry, which deals almost entirely with solutions in one solvent or another.

When we turn to physics we find solutions not playing as prominent a rôle as in chemistry, but nevertheless coming in many places. The primary cells, secondary cells, electrolysis, polarization, diffusion, viscosity, surface tension, are all phenomena in which the physicist is interested and all depend for their existence upon solution.

When we turn to the biological sciences we find that solution is almost as important as for chemistry. Take physiology —here we have to deal very largely with solution in the broad sense of that term. The same remark applies to physiological botany, and solutions are very important for both animal and vegetable morphology, especially in their experimental developments. Bacteriology is fundamentally connected with solutions, and pharmacology is based upon solutions either without or within the body of the animal.

Solution in the broad sense is as fundamental for geology as for chemistry. The igneous rocks were solutions of one molten mass in another, and sedimentary deposits came down for the most part from solutions in water. The minerals crystallized out from solutions, and solutions of various substances, such as carbon dioxide, are to-day weathering the rocks and continually changing the appearance of the face of the globe.

An examination of facts such as those referred to above will show the truth of the statement that the relation of physical chemistry to solutions is the prime reason why physical chemistry is so closely related to so many other branches of natural science.

This alone would show the importance of a true and comprehensive theory of solutions not alone for physical chemistry but for the natural sciences in general.

Description of Plates VIII to XXIV.

Plate VIII. *A.* Uranyl and Zinc Chlorides in Water.
Concentration of uranyl salt, 0.2 normal. Zinc salt, saturated.
Depth of cell, 3, 6, 12, 24 and 35 mm.

B. Uranyl Chloride and Hydrochloric Acid.
Concentration of uranyl chloride, 0.2 normal. Hydrochloric acid, very strong.
Depth of cell, 3, 6, 12, 24 and 35 mm.

Plate IX. *A.* Uranyl Chloride in Glycerol. Cell depth, 10 mm.
Concentrations, 0.176, 0.132, 0.088, 0.059, 0.041, 0.030, and 0.022 normal.
B. Uranyl Chloride in Glycerol. Cell depth, 5 mm.
Concentrations, 0.176, 0.132, 0.088, 0.058, 0.041, 0.03 and 0.022 normal.

Plate X. *A.* Uranous Bromide in Methyl Alcohol. Depth of cell, 3, 6, 11 and 16 mm.
B. Uranyl Nitrate in Water to which Hydrobromic Acid is Added.
C. Mixtures of Uranyl Nitrate and Uranyl Sulphate in Water.

	Strip 1.	Strip 2.	Strip 3.	Strip 4.	Strip 5.	Strip 6.
Uranyl nitrate (per cent.)	100	80	60	40	20	0
Uranyl sulphate "	0	20	40	60	80	100

Plate XI. *A.* Uranous Acetate to which Nitric Acid is Added.
B. The first four strips give the effect of adding hydrochloric acid to a nitric acid solution of uranyl nitrate. The remaining strips represent the same effect obtained by using a greater depth of cell.

Plate XII. *A.* Uranyl Nitrate to which Acetic Acid is Added.
B. Uranyl Nitrate in Water to which Sulphuric Acid is Added.
Cell depth, 8 mm.

Plate XIII. *A.* Uranyl Nitrate in Water to which Sulphuric Acid is Added.
B. Uranyl Nitrate in Water to which Acetic Acid is Added.

Plate XIV. *A.* Uranous Chloride in Water. Concentration constant. Cell depths, 1.2, 2, 4, 8, 16 and 32 mm.
B. Uranous and Aluminium Chlorides in Water.
Cell depths, 1.2, 2, 4, 8, 16 and 32 mm.

Plate XV. *A.* Uranous Chloride in Glycerol and Mixtures of Glycerol and Water. The first strip represents the absorption of a 6 mm. solution of uranous chloride in glycerol. Succeeding strips show the effect of the addition of water.
B. This is exactly similar to *A* except that methyl alcohol was added instead of water.

Plate XVI. *A.* Uranous Chloride in Methyl Alcohol. Concentration constant.

B. Uranous Acetate in Methyl Alcohol. Concentration constant.

C. Uranous Chloride in Glycerol. Concentration constant.

Cell depths, 3, 4, 6, 9, 13, 18 and 24 mm.

Plate XVII. *A.* Uranous Chloride in Acetone.

Cell depths, 5, 6, 8.3 and 15 mm. The first strip represents uranous chloride in acetone, and the following strips the same to which hydrochloric acid has been added.

B. In this case uranyl chloride instead of uranous chloride was used. Cell depths, 2, 3.4, 4, 5, 11 and 30 mm.

C. Strips 1, 2 and 3 represent the same effect as *A*.
Strip 4 represents an ether solution of uranous chloride.
Strips 5, 6 and 7 represent absorption of 2, 5 and 14 mm., respectively, of uranous chloride in acetone.

Plate XVIII. *A.* Uranous Bromide in Methyl Alcohol.

B. Uranous Acetate to which Nitric Acid is Added.

Plate XIX. *A.* Uranous Bromide in Water, Beer's Law Test. The first solution consisted of an 0.8 mm. layer to which water was added to make the depth 2.8, 6, 12.5, 22 and 35 mm.

B. Uranous Bromide in Glycerol, 0.06 normal concentration.

Cell depths, 5, 7.5, 10, 15, 20, 26 and 33 mm.

Plate XX. *A.* Uranyl Nitrate in Nitric Acid to which Sulphuric Acid is Added.

Cell depths, 8, 8.4, 9, 12 and 17 mm.

B. Uranous Acetate in Acetic Acid to which Hydrobromic Acid is Added.

Cell depths, 22, 22.3, 24, 30 and 36 mm.

Plate XXI. *A.* An Acid Solution of Uranous Chloride to which Ethyl Alcohol is Added.

Cell depths, 4.5, 5, 7, 15 and 35 mm.

B. Uranous Chloride in Water to which Acetic Acid is Added.

Depths of cell, 5, 5.8, 7.5 and 26 mm.

Plate XXII. *A.* Uranous Chloride in Acetone. Depth of cell varied.

B. Uranous Chloride in Methyl Alcohol.

Depths of cell, 2, 4, 6, 8 and 12 mm.

C. Uranous Chloride in Glycerol.

Depths of cell, 2, 4, 6, 8, 12 and 24 mm.

Plate XXIII. *A.* Uranous Chloride in Water to which Ethyl Alcohol is Added.

Cell depths, 3.2, 4.4, 6.4, 12 and 22.5 mm.

B. Uranous Acetate in Water.
Cell depths, 3, 6, 12, 24 and 35 mm.

C. Uranyl Acetate in Acetone and Acetic Acid.
Cell depths, 3, 6, 12, 24 and 35 mm.

Plate XXIV. *A.* Uranous Chloride to which Concentrated Aluminium Chloride is Added.

Strip 1, 3 mm. uranous chloride and 1 mm. aluminium chloride; strip 2, the same and 2 mm. aluminium chloride; strip 3, the same and 10 mm. aluminium chloride; strip 4 is a 3 mm. solution of uranous chloride; strip 5 is the same to which 13 mm. strong hydrochloric acid is added.

B. (1) Uranous chloride in water, 4 mm.; (2) plus methyl alcohol to 6.3 mm.; (3) plus methyl alcohol to 7.5 mm.; (4) uranous chloride in water, 4 mm.; (5) the same plus acetic acid to 28 mm.; (6) four mm. uranous chloride in water plus 2 mm. nitric acid; (7) four mm. uranous chloride in water plus 19 mm. sulphuric acid.

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PHYSICAL CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY,
October, 1910.

HELIX CHEMICA.

A STUDY OF THE PERIODIC RELATIONS OF THE ELEMENTS AND THEIR GRAPHIC REPRESENTATION.

By B. K. Emerson.

CHAPTER I.

Chancourtois, the first to propose a spiral arrangement of the elements in the order of their combining weights, was a geologist, and the writer has long used a modification of Crookes's double spiral[1] with students in geology in considering the "first things"—its first culmination in carbon, the vital element, its second in silicon, the earth element, and the iron-nickel group just below all having a peculiar suggestiveness.

The eccentric position of the Siamese-twin groups of the "eighth series" seemed an imperfection in Crookes's spiral and the writer was led to devise the helix described in this paper from a discussion of the subject with his colleague, Professor Hopkins, in which the latter explained the important valence-volume curve upon which he was working.[2]

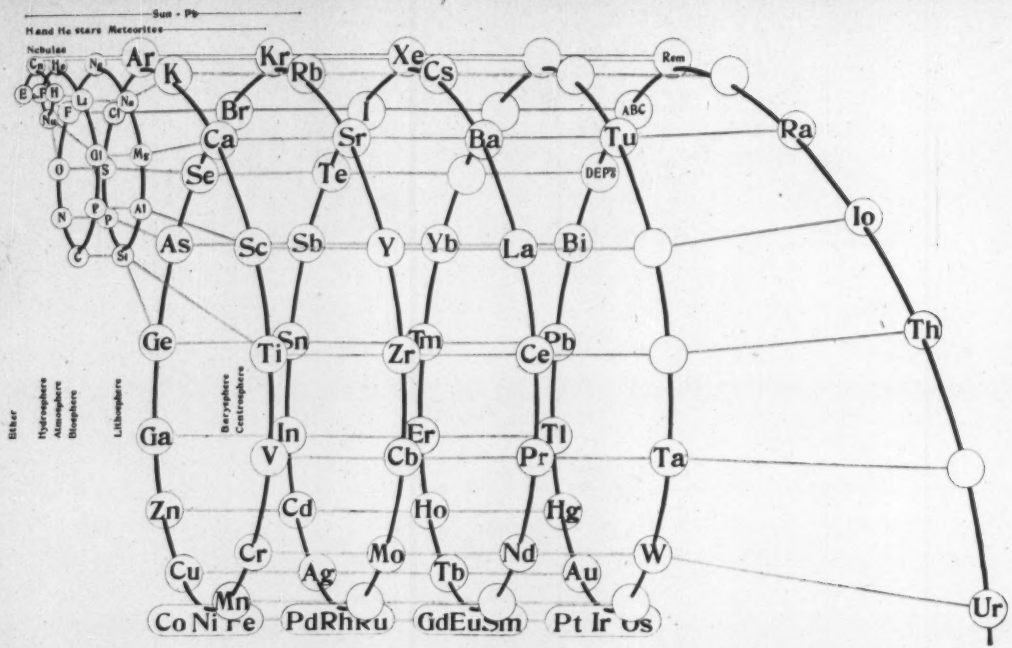
This curve emphasizes the important point that, while in the short periods the specific gravity rises from about 1 to 4, from lithium to carbon, or from sodium to silicon, and decreases to fluorine or chlorine, thus agreeing with the valence, from potassium through titanium, and in the later groups, the specific gravity rises parallel with the rise of the valence from 1 to 8.

From this came the idea of retaining the two short series in the old form of the Crookes spiral, with an amplitude of 4, or as octaves, and drawing the four long series with an amplitude of 8 as double octaves.

Very quickly the suggestion came to continue the curve backward to include hydrogen as a half-octave, preceded, finally, by a quarter-octave which ends at the origin of the

[1] Chem. News, **67**, 217 (1888).

[2] A. J. Hopkins: Science, **28**, 220 (1908.) Preliminary paper read at the Hanover meeting of the American Chemical Society, July, 1908.


Sun + Pb
H and He stars Meteorites
Nebulae
Ether
Hydrosphere
Atmosphere
Biosphere
Lithosphere
Barysphere
Centrosphere
Ar
K
Kr
Rb
Xe
Cs
Rem
Br
Ca
Sr
Ba
Tu
ABC
Ra
Se
Te
DEPs
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Sc
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Er
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Zn
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Mn
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Co Ni Fe
Pd Rh Ru
Gd Eu Sm
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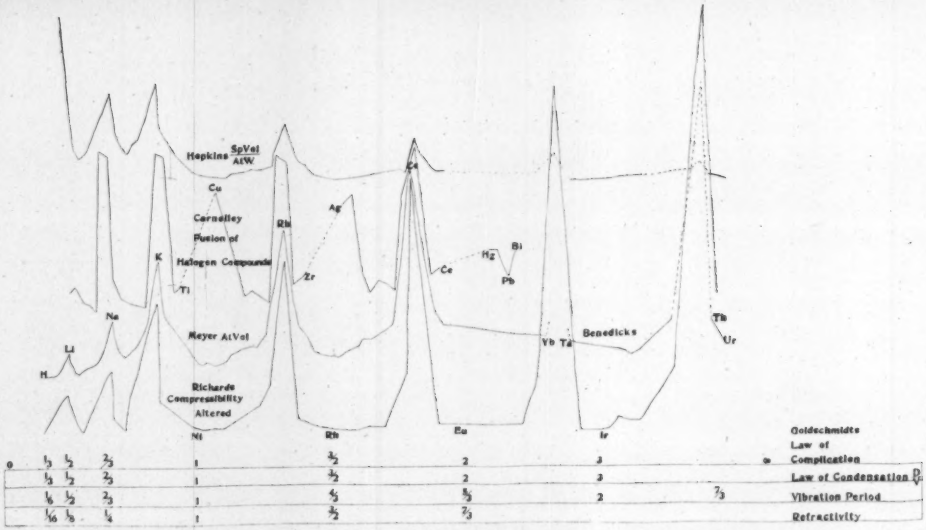

FIG. I.—A side view of the helix drawn to scale for me by A. L. Kimball, Jr. The four graphs below have been changed, in size only, to match the diagram. It will be seen that the apices of the same point exactly to the alkalis and match closely the four double octaves, the two octaves, and the half-octave. The table showing the longitudinal octave relations is placed below.

The atomic volume graph has been completed on Fig. V., in accordance with the calculation on page 184, and if the emended graph had been drawn its eight apices would have matched exactly the eight inert gases.

For fusion of halogen compounds see page 193; for Meyer's atomic-volume curve, page 183; for compressibility, page 186; for the law of complication and condensation, page 176; for vibration period, page 178; and for refractivity, pages 177, 195.

[In the text and the other figures accompanying this paper Proto F is used instead of Eka F.]

curve. In the other direction the helix was completed as a quadruple octave. The result was a spiral with increasing amplitude, in which all the loops are on one side and are drawn with a common axis passing through the line of the inert gases. In Figs. I and II this helix is represented from the side and in Fig. III it is drawn from the end. It is placed horizontally to bring the gases uppermost, the heaviest metals lowest, and so that the downward sweep of the curve is in the direction of the greatest compression. This brings it into a position harmonizing exactly with the curves of atomic volume, of specific volume, of compressibility, etc., as in Fig. I. In Fig. III*a* the same curve is drawn in a slightly false perspective: the four large circles which should really hide each other are drawn like four hoops on the end of a barrel, while the two smaller circles appear like hoops on a smaller barrel. This first free-hand curve I have not been able to improve materially, and so it has been copied on subsequent figures, as a background, on which to reproduce on a common scale many of the more intricate relations separately.

CHAPTER II.

The Helix.

1. The Origin.—At the origin of the curve is "der Urstoff," the "Protyle" of Bacon, the Ether or Electron, E, with valence and density equal to zero.[1] This is deduced below from the identity of the law of longitudinal condensation and the law of complication (see. p. 176). We may almost say, also, with an atomic weight of zero, since E is the x of Mendeléeff for which he deduced a hypothetical atomic weight one-millionth that of the hydrogen atom.[2]

It is difficult to discuss the elements without using language which indicates that they have been derived each from its predecessor. While this evolution has not been yet observed, the opposite devolution is exemplified in the derivatives of radium.

[1] G. J. Storey: On Texture in Media and on the Nonexistence of Density in the Elemental Ether. Phil. Mag., [5] **29**, 467.

[2] Chemistry, English Edition, 1905.

We may thus take ether to be not an element but the origin of all the elements.

2. The Initial Half-Circle.—The curve rising from ether to coronium (see Figs. I and III) represents by its length and direction the passage of a group of ultimate corpuscles or electrons into a simplest element. Its length is proportional to the atomic weight of coronium; its direction indicates expansion.

Coronium present in the corona of the sun is drafted into this first position since it is supposed to be a very light and inert gas.[1]

There is spectroscopic evidence that coronium has a lower atomic weight than hydrogen, for the lines due to its presence in the solar gases can be observed further from the sun than those of hydrogen.[2]

It must have, from its position in the row of the inert gases on the helix, a valence equal to zero and a specific gravity that permits it to be condensed into hydrogen, whose specific gravity is 0.086. Its refractive index may be about 36 (see page 178).

It occupies the position of the second element y extrapolated by Mendeléeff,[3] for which he obtains a possible atomic weight of 0.4. By the same method, but taking closer account of the change in the ratios (which are enclosed in brackets in the table below), we obtain the value 0.3.

$$\frac{Ca}{Mg} = 1.6\ (1.1)\ \frac{K}{Na} = 1.7\ (1.2)\ \frac{Ar}{Ne} = 2$$

$$\frac{Mg}{Gl} = 2.67\ (1.2)\ \frac{Na}{Li} = 3.28\ (1.5)\ \frac{Ne}{He} = 5$$

$$\frac{Li}{H} = 7\ (1.9)\ \frac{He}{y} = 13.3\ y = 0.3$$

The symmetry of the helix would suggest a still smaller number near zero (see page 168). The position of coronium is a

[1] See G. F. Becker: Relations of Radio-Activity to Cosmogony. Bull. Geol. Soc. Am., **19**, 125 (1908).

[2] A. E. Garrett: The Periodic Law (1909), p. 243.

[3] Chemistry, English Edition, 1905. A. E. Garrett: The Periodic Law (1909), p. 241

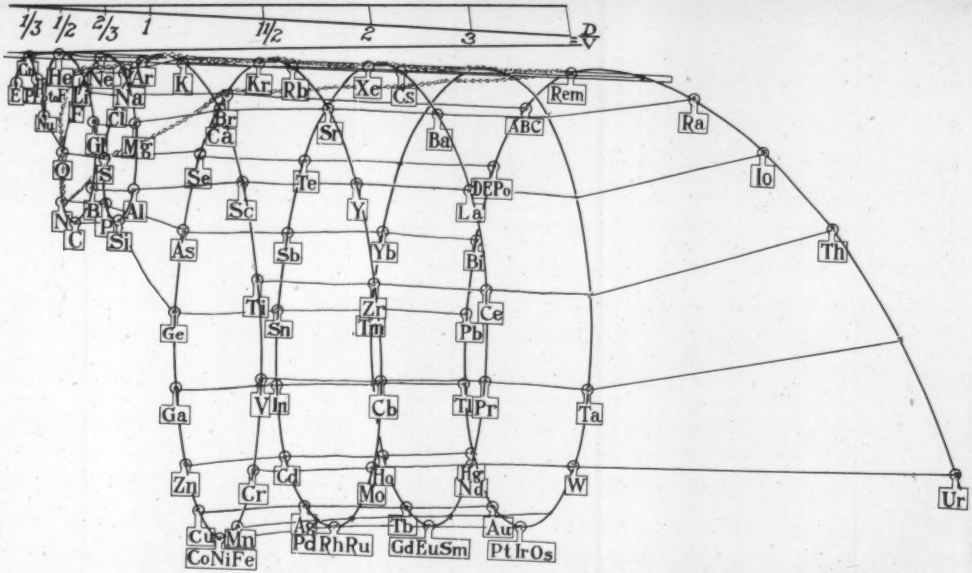

FIG. II.—From a photograph of a model of the helix constructed for me by A. L. Kimball, Jr., and R. D. Eaglesfield.

A chain is placed at the lower boundary of the gas area, but the camera had to be so placed to prevent the letters overlapping that it is not well seen. The front half is concealed by the rod. It can be seen to pass in front of Ar, Ne and He, then to bend down to include F, O and N, and then to rise in the rear of the figure to graze Br.

The model is depressed to the right to bring this chain into the horizontal position of a contour line.

The amount of this depression is indicated by the acute angle placed above the diagram, and the numbers represent the longitudinal increase in density. It is as if the heavier end of the series at the right had sagged by this amount, bringing the elements below the area where the gaseous condition is possible. See *The Gas Area*, page 187.

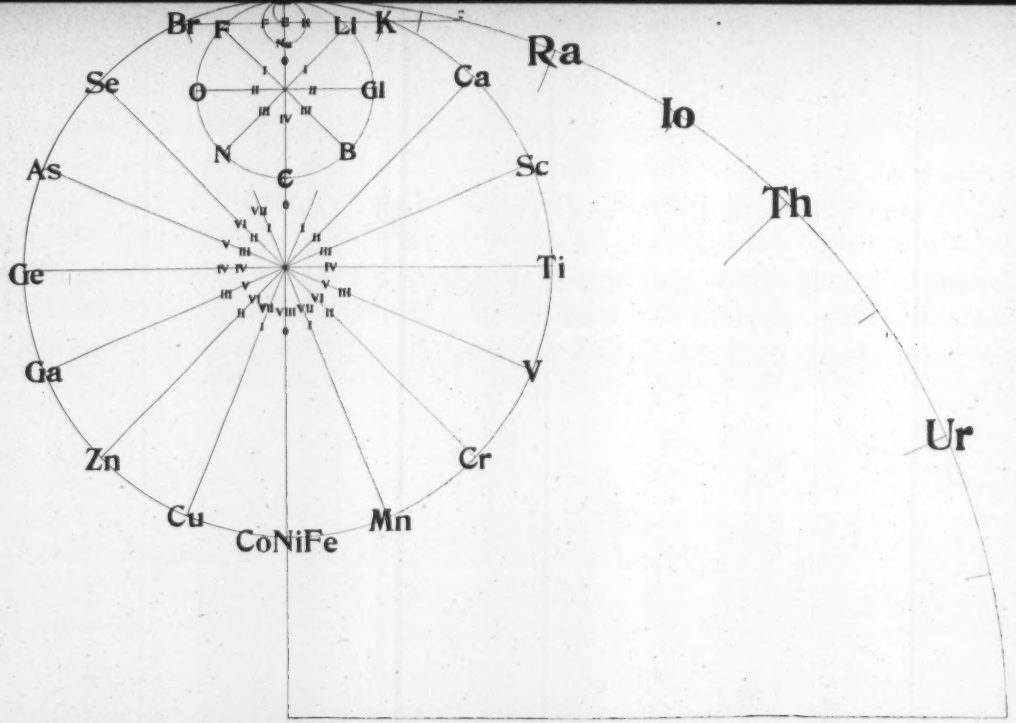

FIG. III.—An end view of the helix in true scale (except the curve E-Cn) showing only the first of the octaves and double octaves and symbolizing the increasing mass of the atoms (see page 197).

[The first V should be

culminating point where the curve passes through zero, and all that is implied by this in mathematics is realized in Nature at this and the subsequent similar passages.

Dilatation and all its consequences are followed symmetrically by condensation and all its consequences.

We may distinguish three possibilities at this point:

1. As water rises in a wave and sinks back into itself, so the coronium formed from the ether might continuously sink back into the ether again. This would be typified by a closed circle with a single vertical diameter, with coron um at the top and ether at the bottom.

2. We may assume the third dimension to enter into the curve and the latter to complete itself without touching the point of origin, and to become a simple helix of this amplitude. The next element produced at the bottom of the curve would have been a monad and there would have followed an alternating succession of monads and nullivalent elements.

This represents a possible condition of a simplest nebula.

3. The Second Circle.—The simple possibilities suggested in the last section were not realized, but in sinking to greater c ndensation from coronium to hydrogen the passage is along a curve of double amplitude. This curve is drawn by taking the curve coronium-hydrogen equal to unity. This is best shown in Fig. III. This second curve is a half-octave bisected by two diameters, horizontal and vertical, giving places at their ends for four elements.

It is as if an added momentum had increased the tangential component of the curve and so extended the circle. This recalls the curious theory of a German chemist, which I have read but cannot locate, that valence depends upon the angle of impact of the elements in combining.

There is a certain completeness in the symmetry which makes the first complete circle quadrated, with four elements at the ends of the diameters, whose combining weights are 1, 2, 3, and 4. At the end of the first quadrant, on the electropositive side, stands hydrogen with the combining weight 1. At the end of the second quadrant must stand a dyad with the combining weight 2. Nebulium, which appears in the nebulae,

is supposed to be somewhat heavier than hydrogen, since it has been found to be more concentrated in the central parts of a nebula than hydrogen,[1] and may stand here. At the third quadrant there must be a univalent element with the combining weight 3, and strongly electronegative. Here I have written protofluorine, since, as the diagram shows, this element stands above fluorine at the head of the halogens. Perhaps it may be among the new constituents of unknown nature found in Uranus and Neptune.[2] It is true of the octaves which follow that the combining weight of an element is always 16 less than that of the element below it; thus, as the combining weight of lithium, 7, may be derived from that of sodium by subtracting 16 from 23, so the combining weight of protofluorine may be obtained from that of fluorine: $19 - 16 = 3$.

At the end of the fourth quadrant stands helium with the combining weight 4, valence 0, occupying the second zero point.

The argument for the existence of such a half-octave is cumulative, and must appear mainly in the subsequent pages and from an inspection of the diagram. Anticipating, it will be seen that there are four double octaves containing sixteen elements each, two octaves containing eight elements each, and this demands one half-octave containing four elements, and the half of a quarter-octave containing one element. This interesting symmetry is more fully explained in Section 7, page 168. An inspection of the curves of atomic volume, of specific volume, and of compressibility (see Fig. I) will show that there are four loops corresponding to the four double octaves, two of half-width like the octaves, and one space of half the latter width remaining for the half-octave. This incorporates Mendeléeff's suggestion of a series including hydrogen, but makes it a short or half-series in which an intensified fluorine alone remains to be discovered.

The distance advanced along the first circle is four (helium = 4), and since four elements find place in this circle the inter-

[1] Svante Arrhenius: Das Werden der Welten (1908), p. 177.
[2] *Loc. cit.*, p. 55.

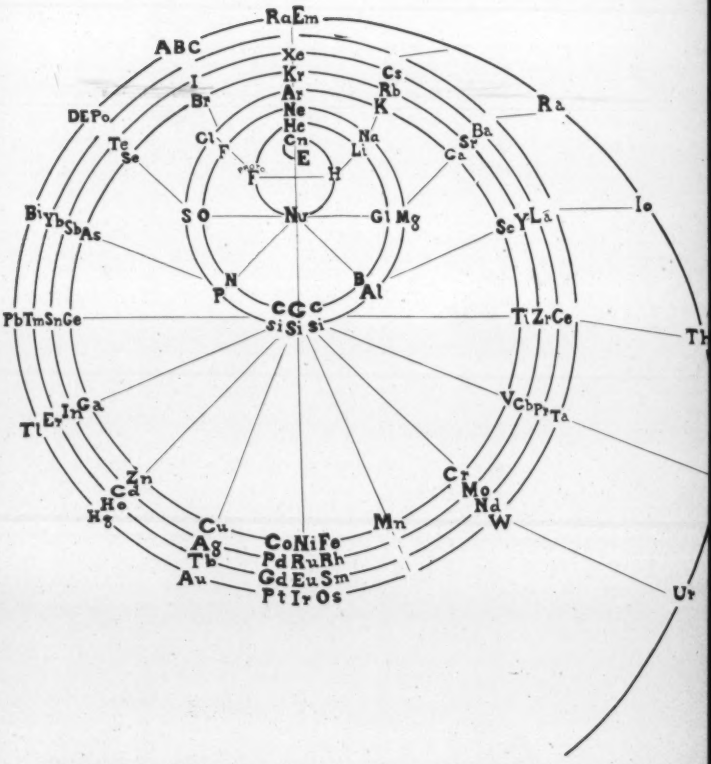

FIG. IIIa.—The helix drawn in false perspective so that the octave rings appear like hoops on the end of a barrel the double octaves like hoops on a larger barrel.

The outer rings are about in the true ratio of 0:1:2:3:4. The groups of Mendeléeff are placed radially the series along the curve. The curve E-Cn is an infinitesimal and E is almost in the line of the inert gases [NOTE.—Copies of this figure may be obtained from the Editor.]

space coronium-hydrogen is one, and the quadrant of this circle has been drawn as unity. We may anticipate the fact that these interspaces average successively 1, 2, 3, 4 for the different groups of circles. These interspaces are really the graphic representations of interweights, and seem to indicate in the half-octave the continuous addition of an assemblage of corpuscles about equal to a unit (or hydrogen) atom; in the octaves the continuous addition of a group equivalent to a dyad (a nebulium atom); in the double octave the continuous addition of a triad (protofluorine atom); and in the outer or radium circle the continuous addition of a quadrivalent (helium) atom, just as the giving off of an α particle is a subtraction of the equivalent of the same helium atom.[1] So perfectly is the half-octave a microcosm suggesting the evolution of the whole series. If the helix had gone on with this amplitude a fourfold succession of elements might have been made with the maximum valence 2. This we may call the nebula condition. See Fig 1, top.

There is some spectroscopic evidence for the existence and proposed arrangement of the half-octave. Of the very simple spectra detected in the simplest nebulae, the lines with wave length 4340 t.m. and 4862 t.m. have been found to belong to hydrogen. The name nebulium has been given to the element showing the next line, 4857 t.m. The next higher number, 5007 t.m., may be tentatively assigned to protofluorine, and the still higher number, 5876 t.m., belongs to helium.[2]

4. *The Construction of the Octave Circles.*—Following the one half-octave come two octaves. In these the elements sink in wonderful symmetry through lithium to carbon and rise through fluorine to neon. They repeat this curve with absolute fidelity through sodium to silicon and on through chlorine to argon. The valence changes from one in the alkalis to two in the alkaline earths, and then on to a maximum of four in carbon and silicon. It decreases regularly

[1] Professor J. J. Thompson accepts the view "that it is by the combination of the atoms of the lighter elements that the atoms of the heavier elements are produced" (Electricity and Matter, p. 126).

[2] A. C. and A. E. Jessup: Evolution and Devolution. Phil. Mag., [6] **15**, 29.

on the upward curve to one in the halogens. Hopkins has insisted on the importance of the fact that the specific gravity is about one in the monads, and rises symmetrically to about four in the tetrads, sinking again regularly in all the solid elements, parallel with the valence.

To form the first octave, we follow along the curve from helium past lithium, and find it completed in neon, and the length of the curve is 16 [Ne (20)—He(4) = 16]. The curve is repeated past sodium to argon, and this distance is also 16. This is the reason for the constant difference of 16 in the combining weights of adjacent elements of the first two series. Since there are eight elements along each of these curves, the length of the interspaces must average two (16/8). Therefore the distance helium-lithium is made twice as great as the unit coronium-hydrogen in the first circle. As the first circle was cut by one diameter and the second by two, these are cut by four diameters, giving place for the eight elements found upon each. Here again the series of circles might have continued indefinitely, making symmetrical octaves with a maximum valence of 4.

5. *The Construction of the Double Octaves.*—When we come to the potassium-calcium circle, there is a radical change. The first four elements are exactly comparable with the first four elements of the two preceding octaves, potassium with sodium, calcium with magnesium, and so on. Valence and specific gravity are also exactly comparable, rising from one in potassium to four in titanium, but the specific gravity and one of the valences continue to increase, reaching each a culmination of eight in the iron group and growing smaller through copper to one in bromine and zero in krypton. This is repeated four times, the elements sinking in a curve of doubled amplitude and frothing four times into a triad group like the spray on the crest of a great wave. Each triad group occupies the place of a single element. It is interesting that carbon and silicon, at the crests of the octaves, by their three marked allotropic forms prophesy these triads at the crests of the double octaves.[1]

[1] J. Emerson Reynolds: Nature, **81**, 206 (1909).

The length of each of these circles, though slightly less regular, is about forty-eight (Sr — Ca = 48, Ba — Sr = 49, etc., etc.). As we drew four diameters in the last circles, we must draw eight here, making places at their ends for sixteen elements in each circle, and sixteen elements are found for these places. The interspace (which was one in the first circle and two in the second circle) here becomes three (48/16).[1]

Since *one* half-octave and *two* octaves are present there should be *four* double octaves, and four are found, nearly complete and symmetrical, beginning with potassium and ending with the radium emanation, Ra Em, which is placed here tentatively, as are the other radium derivatives.[2]

6. The Quadruple Octave.—The symmetry which limits the number of the preceding double octaves to four is a principal argument for postulating a quadruple octave for the radiant elements. Moreover, the average interspace or change of weight is almost exactly four, completing the series of interspace numbers 1–2–3–4, and the α particles have an atomic weight of four.

The elements of the half-octave are sufficiently peculiar. They are the nebulae makers. Hydrogen has been a waif and stray ever since the periodic system was proposed. The octave elements have long been isolated as the "normal elements," and the double octave elements have, especially in the higher valence semicircle, many common peculiarities. In the same way, the few elements that represent the still larger circle are separated by their spontaneous decomposition, their high combining weight, and in many other ways, from the preceding groups.

As we drew eight diameters in the last circle we must draw sixteen here, and we may assume that thirty-two elements would normally find place on one of these circles at the ends of these diameters, and as the number of the circles has increased in geometrical progression the number of these larger circles should be eight.

[1] The line of the curve runs through the rare elements with great uncertainty, like the broken line of history through the dark ages, when there was more alchemy than chemistry.

[2] Newly called Niton, atomic weight 221. Nature, **1910**, 517.

The helix is thus a multiple series of circles increasing *per saltum*, beginning with an origin at E and continuing *ad infinitum*; but in the last group only the first quadrant of the first circle is present, the helix being limited in this direction by the great complexity of the atom, which falls apart spontaneously; just as the schoolmen explained that there were no animals larger than the elephant, because, if they had been created, they would have collapsed of their own weight.

7. *Tabular Representation of the Symmetries of the Helix.*—The symmetrical relations of the helix which have been explained in the preceding pages are brought together in the following table. These relations have been deduced directly from the atomic weights and the recurring similarities of the elements. The ideal serial positions of the elements are found to be symbolized by the simplest harmonic relations of the simplest increasing series of circles.[1]

As the atomic weights of the elements have been found not to be whole numbers, so the interweights which are represented by the interspaces in Column 1 would not be whole numbers but close averages, and the first one would not be zero, but some very small number. See p. 162.

It is interesting that while the lengths of the interspaces are in the simplest arithmetical ratio, all the other relations are in the same simplest geometrical ratio, *viz.*, the number of interspaces, the number of circles, and, if we consider ether an element, the number of elements in each circle; while the length of the circles is obtained by combining these two ratios.

[1] As the last circle is so incompletely represented, it was not at first apparent what was the continuation of the curve, and three other alternatives were considered; and it is interesting to present them for comparison with the chosen arrangement, which seems to be the true one.

In one case the last half-curve containing uranium was supposed to be identical with the preceding ones. This ignores the regular progression (which would demand four double octaves only) and the increased interspace.

A second case was suggested by the fact that radium, thorium, and uranium occupy every other space, making possible an octave (that is, eight elements) on a fifth circle of the same size as the preceding one, followed by a circle of the same size on which every fourth space was occupied. The location of ionium militates against this.

A final case suggests an arrangement of too ideal symmetry, where the coil ends as it begins; with two octaves followed by one half-octave. It brings uranium round into the electronegative position.

	Quarter-octave.	Half-octave.	Octaves.	Double octaves.	Quadruple octaves.	
(1) Length of interspace (= interweights) in each type of circle (approximate). Unit curve = Cn—H	0	1	2	3	4	Simplest arithmetical ratio.
(2) Number of interspaces in each type of circle	2	4	8	16	32	Simplest geometrical ratio.
(3) Number of elements in each type of circle	2	4	8	16	32	
(4) Number of circles of each type	1/2	1	2	4	8	
(5) Number of elements in each circle, obtained from (4) and (2)	1	4	8	16	32	
(6) Length of each type of circle, obtained by multiplying preceding ratios in (1) and (2)	0	4	16	48	128	Combination of above.

8. As to the Length of the Axis of the Helix.—It is natural to think of the helix as a real entity and to ask what is the distance between the successive curves. Indeed, I have spoken above of the third dimension asserting itself, so that the second circle did not coincide with the first and so formed a helix, instead of a flat spiral. As an expression of the symmetries concerned, there must be at least an infinitesimal distance between these curves.

The conditions imposed by the numbers in the preceding table would seem not to fix this distance. If we imagine the wire of the helix in Fig. II to be pierced with holes through which the axis runs, the helix could be drawn out or compressed by sliding along the axis, without disturbing the relations expressed in the above table.

The model in Fig. II was constructed by giving a convenient length to the distances between the double octaves, and half and a fourth of that for the whole and half-octaves. It would be perhaps best to have these distances proportional to the differences between the atomic weights of the elements located along the axis, though this relation has also been used to determine the length of the circles.

9. Atomic Weight Differences as Evidence of the Correctness of the Proposed Arrangement.—Pettenkofer's suggestion of the constant differences between analogous elements finds such full expansion and explanation when applied to the present arrangement as to form a practical proof of the correctness of the arrangement itself.

In the octaves there is a constant difference of sixteen (Si — C = 16, Ne — He = 16, etc.), and in the double series a constant difference averaging close to forty-eight. In passing through potassium and calcium the circles diverge and the differences gradually increase from 16 to 48 (K — Na = 16, Ca — Mg = 17, Co — Si = 30, Br — Cl = 45). An inspection of the diagram (Fig. III*a*) shows the reason for this increase to be as follows: While from neon around to argon the distance is wholly in the smaller circle (16), and from argon to krypton wholly in the larger (48), any subtraction made between members of the second octave (the sodium series) and the first double octave (the potassium series) will be measured in part on the short circle and in part on the long circle, and so will give a succession of numbers increasing from sixteen to forty-eight, as the distance passes entirely to the long circle. It will be seen that the increasing distance in the diagram between the half-octave and the octave, and between the octave and the double octave, is exactly parallel to the differences in the atomic weights of the corresponding pairs of elements.

The results reached from the smaller circle, although partly surmise, are of curious interest. Starting from H = 1, we assume Nu = 2, as it gives indications of being heavier than hydrogen, and Proto F = 3 [F(19) — 16 = 3] and find He = 4. This gives the proper difference, 16, for F — Proto F, and

the difference decreases regularly (O — Nu = 14, N — Nu = 12, C — Nu = 10, B — Nu = 9, Gl — Nu = 7) until we find Li — H = 6, and the assumption for coronium of a very small fractional combining weight would make He — Cn near 4.[1]

A further inspection of Fig. III*a* would suggest that if Ne — He = 16, F — Proto F should be less than 16, but a comparison with Fig. X will show that the undue symmetry of the diagram is here misleading, and that in reality fluorine and all the halogens are placed so near the inert gases that the distance would be near 16.

Finally, if the last circle were of the same dimensions as the preceding, the atomic weight differences between elements in the same horizontal series would still be 48. If the circle is enlarged and the normal interspace between successive elements along the circle is four instead of three, each difference after passing the zero line at radium emanation should be increased by one unit because of the increased interspaces. It will be seen from the table below that the observed differences are closely what would be expected with the enlarged circle:

Elements in fifth circle	Ra Em	..	Ra	Io	Th	....	Ur
Corresponding elements in fourth circle	....	..	..	..	..	....	Ta
Ideal differences with the last, or fifth, circle of the same size as the four preceding ones	48	48	48	48	48	48	48
Ideal differences with enlarged fifth circle	48	49	50	51	52	53	54
Observed and calculated differences	48	47	55	52	52	52·5	54·5

The most probable values of the atomic weights, obtained by adding 3 to the corresponding element on the third circle, were taken for the unknown elements in the lower row, and subtracted from those of the elements in the upper row to

[1] This makes the position of hydrogen at the head of the alkalis more probable than at the head of the halogens, and at the same time approximates hydrogen and protofluorine so closely, and so entirely without the possibility of an intervening element ("E" is not an element) that the question becomes a subordinate one in a certain sense.

Hydrogen is also electropositive, and so more naturally at the head of the alkalis. See Orme Masson (Chem. News, **73**, 283) who marshals the arguments in favor of placing hydrogen at the head of the halogens.

obtain the observed differences given, except, of course, in the case of uranium—tantalum, and the result agrees quite exactly with the assumption of an enlarged circle.

10. The Table of the Periodic Law.—The table expressing the periodic law is most logically obtained, in the usual form of horizontal groups and vertical series, by letting the radius vector, passing from the center of the helix at E (see Fig. III*a*) through the inert gases, move in the direction of advance along the curve producing the table of the elements given on the following page. This table is perhaps the best arrangement of the elements possible on a plane surface.

It is most closely approached in the paper of Cuthbertson and Metcalfe, discussed on page 177. It is very useful for the presentation of some of the serial relations of the elements, but for the clear exhibition of many symmetries is greatly inferior to the helix, which has the advantage of three dimensions.

This is especially the case with regard to the odd and even series of Mendeléeff, which are approximated in his table with a certain unnatural naturalness, but are placed as far apart as possible on the helix, each pair, as potassium and copper, being at the opposite ends of a diameter. Their approximation in the Mendeléeff table is as when two points on the opposite sides of a hollow ball are brought together by the collapse of the ball. They are approximated because the respective heavy metal series *can* be monovalent, while in most respects they are the opposite of the light metal series. The copper-gold series stands as the antithesis—the "Spiegelbild"—of the alkali series. Copper and gold *can* be monads, but they are passing from a zero valence at the point of magnetic maximum and least compressibility and incipient dilatation, while the alkalies *must* be monads, and they hold a symmetrical position in relation to the opposite zero point in the area of greatest compressibility and beginning condensation. It is the same with the scandium series as compared with the gallium series.

The monovalency of the alkalies is grounded on the fact that they have one free electron to be given up, while the halogens are monovalent in that they are ready to take up one electron.

Periodic Table of Atomic Weights.

E																Proto F
Cn	H	Nu														
He	Li	Gl	B	C										N	O	F
Ne	Na	Mg	Al	Si										P	S	Cl
Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	Ge	As	Se	Br
Kr	Rb	Sr	Y	Zr	Cb	Mo	..	Rh	Ru	Pd	Ag	Cd	In	Sn	Sb	Te	I
Xe	Cs	Ba	La	Ce	Pr	Nd	..	Sm	Eu	Gd	Tb	Ho	Er	Tm	Yb	Lu	...
..	..	..	..	..	Ta	W	..	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	ABC
Ra	Em	ThX	Ra	Io	Th	Ra-Ur	Ur										
O	I	II	III	IV	V	VI	VII	VIII			VII	VI	V	IV	III	II	I
					III	II	I	O			I	II	III				

CHAPTER III.

General Relations of Symmetry.

Evidence of the naturalness and value of the helix is found in its use for the statement, comparison and discovery of complex relations among the elements as shown in Figs. IV, VII to IX and X to XII.

Many curious relationships, some homologies, some analogies, and some remote suggestions crowd these figures.

The main symmetry relations can be divided into four classes, though frequently several of these appear together as functions in one harmonic series. These classes are:

(*1*) *Longitudinal* relations, changing parallel with the axis of the figure.

(*2*) *Transverse* relations, changing at right angles to the backbone of the figure, and in this case they may be:

(*2a*) Symmetrical to the median vertical plane, and may be called *meridional* relations; or

(*2b*) Symmetrical to the horizontal plane, *equatorial* relations; or

(*2c*) Symmetrical to a plane placed 45° to the right of the vertical, and called *ecliptic* relations.

In many cases the change is fourfold, being controlled by both the meridional and equatorial planes, and may be called

(*2d*) *Quadrantal* relations.

Similar properties may be confined to the quadrants formed by the ecliptic and the vertical to the same, and may be called

(*2e*) *Ecliptic quadrantal* relations.

A group of allied, but unclassifiable relations are assembled on Fig. IX. They are associated in description with the group to which they are most nearly allied.

SECTION I.—RELATIONS WHICH ARE BOTH LONGITUDINAL AND TRANSVERSE.

1. Condensation and Expansion.

a. The Law of Transverse Condensation and Expansion.—This is the fundamental meridional relation. See Fig. IV.

In passing downward along each curve from an inert gas past an alkali there is a gradual condensation, as is indicated

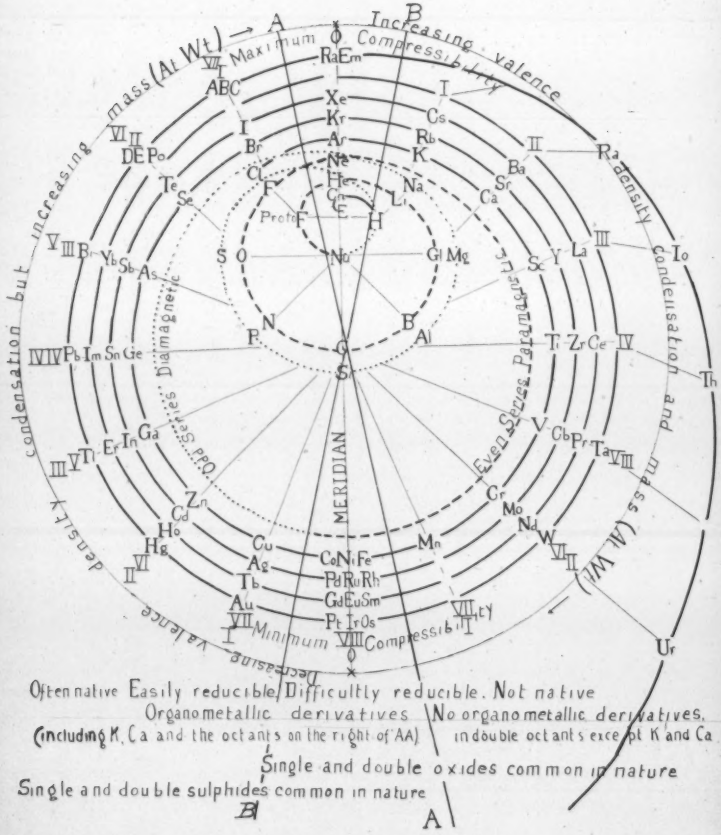

FIG. IV.—Meridional Relations. Part of these relations are strictly meridional; part divide on the line *A A* which passes *to the right of* C and Si; part divide on the line *B B*, which passes *between* C and Si.

For condensation, see page 174; for magnetism, page 182.

by the increasing specific gravity and valence. In passing upward along the last half of the curve from a triad to a halogen there is a corresponding expansion, indicated by decreasing density and valence.

The potassium curve is in every way the central curve, and in passing down it the specific gravity increases regularly from near 1 at potassium to about 8 at iron, agreeing with the valence. In the ascending half of the circle there is a similar but less perfect agreement between the decreasing specific gravity and the valence or position number. A similar change occurs in the other circles. This is clearly expressed on the valence-volume graphs of Professor A. J. Hopkins,[1] who finds for each series the quotient

(*valence*)/(*sp. gr.*) or (*position no.*)/(*sp. gr.*)

to be nearly a constant, and to be thus expressed by horizontal lines.

If we assume the molecules to be of the same size, there is then a twofold, threefold, and at last an eightfold condensation, which may be called the transverse condensation.

If the atom shows its greatest valence, all its attractive force is directed outwardly; if a lower valence, part of its energy is potentialized internally.

When the valence becomes thus multiplied and uncertain it is of little greater value than density in determining the "position" of an element in the series (see Chapter IV, p. 197).

We can realize how, with the addition of equal quantities of matter (equal groups of corpuscles), by a certain internal condensation, or self-condensation, elements may be formed with density and valence increasing from one to four or from one to eight. It is more difficult to conceive how, by the continued addition of matter of the same kind and in the same quantity, the curve should be continued by elements of regularly decreasing density and valence and that this alternation should be repeated rhythmically more than seven times. It may remotely suggest Tamman's[2] law in accordance with which the melting points of many compounds rise with increasing pressure to a

[1] *Loc. cit.*, p. 160.

[2] G. Tamman: Krystallizieren und Schmelzen (1903), p. 184ff.

maximum and then, while the pressure continues to increase, sink gradually to a minimum.

b. The Law of Longitudinal Condensation: (Density)/(Valence) or (Density)/(Position No.) (Fig. I).—In addition to the transverse condensation there is also a longitudinal condensation. It is only in the central curve that valence and density agree from 1 in potassium to 8 in iron, so that $D/v = 1$.

The densities of the iron, rubidium, samarium, and platinum triads are as 8 : 12 : 16 : 22+, or D/v is as 1 : 1.5 : 2 : 3, and this, if we omit gases and poorly determined values, is true of each of the series of which the triads are a sample. Thus in the first or carbon octave we get, omitting oxygen and glucinum, which is always abnormal, an average value for D/v of 0.52; in the second or silicon octave, from sodium to phosphorus, 0.80. In the remaining circles, taking the right-hand or descending semicircle, we have (omitting two abnormal values) for the central or iron circle, 0.99, for the rubidium circle, 1.5, for the samarium circle, 1.92, and for the platinum circle, 2.9. These round up without forcing to

E	Nu	C	Si	Fe	Ru	Sa	Pt
(0)	($^1/_3$)	$^1/_2$	$^2/_3$	1	$^3/_2$	2	3

This represents a gradual longitudinal condensation of each series, superimposed on the transverse condensation explained in the previous section. It is an interesting case under Goldschmidt's "Law of Complication."[1] This permits us to extrapolate the value 1/3 for the nebulium ring, representing the density of its elements in solid form, and zero for the origin E (see p. 161). These values are compared with other similar ones on page 197 and in Fig. I. This result may also be deduced from Hopkins's valence-density graphs.[2] It will be seen in these graphs that while the one containing potassium lies on the unit line, the first two lie above it, and the last four sink gradually below it, and in each case by distances which are proportional to the numbers deduced above.

In accordance with Goldschmidt's Law of Complication, the

[1] Dr. Victor Goldschmidt: Ueber Harmonie und Complication, Berlin, 1901. W. H. Hobbs: Popular Astronomy, **148**, p. 345. Ann Arbor, 1907.

[2] *Loc. cit.*

Law of Longitudinal Condensation coincides not only with the law of the Octave in Music, but also with the fundamental law governing the order and frequency of the appearance of forms in crystals.

In Fig. II the model is made to sag in proportion to this increasing density to explain the gas area (see p. 187).

2. Refractivity (Fig. VIII).

a. The Longitudinal Element of Refractivity.—The valuable article of Cuthbertson and Metcalfe[1] on the refractivity of the volatile elements gives the following table for refractivities:

						H
						139
					He	
					72	
					144 × 1/2	
			N	O	F	Ne
			297	270	192	137 × 1
			P	S	Cl	Ar
			1197	1101	768	568
			299 × 4	275 × 4	192 × 4	142 × 4
Zn	Ga	Ge	As	Se	Br	Kr
2060			1550	1565	1125	850
303 × 6			258 × 6	261 × 6	187 × 6	142 × 4
Cd	In	Sn	Sb	Te	I	Xe
2627			2675	2495	1920	1378
267 × 10			267 × 10	249 × 10	192 × 10	138 × 10
Hg						
1866						

My colleague, Professor A. L. Kimball, has been so kind as to calculate for me the refractivities of other elements expressed in the same form, $(u - 1)\,10^6$, and when these are all plotted on the helix the number for hydrogen comes below that for helium and then the series of factors expressing the longitudinal refractivity is complete as follows:

$^1/_4(?)$ $^1/_2$ 1 4 6 10

This extends the law to the outer half of the alkali series. This regular and common increase of refractive power in passing longitudinally along each of the series, as the halogens

[1] Phil. Trans., A, **207**, 135 (1907).

or inert gases, is extremely interesting, as it finds expression after swinging hydrogen into its place with the alkalies.

Dividing the above row of factors by four to make it comparable with the row expressing the longitudinal compression, we have:

Coefficients of compression	(1/3)	1/2	2/3	1	1 1/2	2	3
Coefficients of refractivity	(1/16?)	1/8	1/4	1	1 1/2	2 1/2	

The similarity of the two series is striking, and can be carried one term farther than appears in the rounded out values, since 2 of the compression series is equal to 2.2 by taking the most favorable values, and 2.5 of the other becomes 2.42 in the same way.

I have permitted myself to extrapolate a possible refractivity, 36, for coronium, which occupies the top of the first circle.

b. The Transverse Element of Refractivity (*Fig. VIII*).—An inspection of the figure shows, in addition to the great longitudinal increase in refractivity, a more moderate transverse variation.

Within the limits of normal refraction the common factor increases either way from a minimum, 140, in the inert gases.

This normal refractivity prevails in the upper three-fourths of the low-fusing semicircle, while the area of colored ions lies just opposite to it in the lower three-fourths of the high-fusing semicircle.

It is thus an ecliptic function and is so treated on page 195 and in Fig. VIII. In the region of expansion, transparency and refraction prevail. In the region of condensation, opacity, absorption and therefore colored ions prevail.

3. Vibration Period(?) (*Fig. I*).

Batschinski[1] has attempted to show that the period of vibration of the elements varies as the square root of the atomic weights. Assuming that the vibrations of the corresponding atoms in the different series must be in some simple and harmonic relation to each other, he suggested as the simplest formula for the period of vibration:

$$T = \pi\sqrt{\frac{m}{g}}$$

[1] A. J. Batschinski: Z. physik. Chem., **43**, 372 (1893).

where m is the mass of an atom, or the atomic weight; g is a constant force-coefficient.

Thus the period of vibration (T) varies as the square root of the atomic weight m. To explain what he means by "vibration" Batschinski states that this formula is based on the assumption that "a frictionless atom is subjected to an attractive force which is the same for all atoms and changes in proportion to its distance from a center."

Curiously, Sutherland has obtained the same ratios independently for the alkalies and alkaline earths, and in part for other series, by the formula

$$p = \left(\frac{M}{d}\right)^{\frac{1}{3}} \frac{(M)^{\frac{1}{3}}}{\sqrt{T}}$$

where M is the mass, T the melting point, d the density.[1]

Batschinski arranged the roots in the order of the elements in Mendeléeff's table, and found that for a part of each series the numbers could be factored into a constant multiplied into the digits 1, 2, 3, 4.

He took this harmonic relation to be the expression of the relative vibration periods of the elements.

Without accepting this conclusion it is interesting to see how much more symmetrical the table becomes when the roots are arranged in our proposed periodic table, and factored so that the numbers in the horizontal column containing potassium become 3, as this expresses the ratio most simply, as given in the table below.

The longitudinal factor increases with remarkable regularity in the simplest arithmetical progression.

In the transverse direction along the line of the helix curve, there is a slow and somewhat regular increase in the constant factor which is, of course, an average, but one of quite closely agreeing numbers.

The controlling function in both the equations cited above is M, or the atomic weight; and it is clear that the table is only another form of expression for the harmonic relations of the atomic weights.

[1] W. Sutherland: New Periodic Property of the Elements. Phil. Mag., [5] **30**, 318.

TABLE OF THE SQUARE ROOTS OF THE ATOMIC WEIGHTS FACTORED INTO A CONSTANT (WHICH IS PLACED BELOW) AND THE SERIES OF NUMBERS IN SIMPLE ARITHMETICAL PROGRESSION.

E

Cn	H	Nu															Proto F	
He	Li	Gl	B	C											N	O	F	
1	1	1¼	1½	1½											1½	1½	1½	
Ne	Na	Mg	Al	Si											P	S	Cl	
2	2	2	2	2											2	2	2	
Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	Ge	As	Se	Br	
3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
Kr	Rb	Sr	Y	Zr	Cb	Mo	..	Rh	Ru	Pd	Ag	Cd	In	Sn	Sb	Te	I	
4	4	4	4	4	4	4	..	4	4	4	4	4	4	4	4	4	4	
Xe	Cs	Ba	La	Ce	Pr	Nd	..	Sm	Eu	Gd	Tb	Ho	Er	Tm	Yb	..	..	
5	5	5	5	5	5	5	..	5	5	5	5	5	5	5	5			
..	..	..	..	..	Ta	W	..	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po		
					6	6		6	6	6	6	6	6	6	6			
Ra	Em	..	Ra	Io	Th	Ac	Ur											
7			7		7		7											
x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	
212	213	226	231	237	232	239	247	244	249	247	250	258	264	275	264	275	292	Constant

It seemed worth while to print it as an additional indication of the naturalness of the order of elements upon the helix, and illustration of the usefulness of the proposed table for the presentation of such relations.

4. Specific Volumes.

Professor Hopkins's graph of specific volume[1] is reproduced in Fig. I, and continued in a dotted line to express the probable relations of the two possible alkalies beyond caesium.

This presents, as Professor Hopkins has shown, the essential relation of the atomic-volume graph of Meyer, given on Fig. I. The latter shows the relation of atomic weight divided by density to atomic weight; the former shows the relation of specific volume or $1/(density)$ to the atomic weight.

Professor Hopkins has shown that in plotting (as is done in Meyer's graph) the atomic weights on the axis of ordinates and the value $(atomic\ weight)/(density)$, or $(atomic\ weight) \times 1/(density)$, on the axis of abscissas, the atomic weight appears actually as a factor in both axes, and produces the same effect as if the axis of abscissas ran upward at an angle of 45°, and the values of the specific volumes (or $1/density$) were plotted with these axes. This explains why in the atomic-volume graph of Meyer the apices of the two first curves at the alkalies lithium and sodium slant upward at a high angle, and those of the remaining ones run upward on a higher but parallel slope. In the specific-volume graph these points are on nearly parallel and horizontal lines, agreeing with the curves of the helix.

SECTION II.—THE MERIDIONAL RELATIONS (SEE FIG. IV, p. 175).

The vertical median plane passing through the zero points is of primary importance. It separates all those values which depend upon the fact that each curve passes from the zero point downward with increasing condensation to a maximum in the triads, and then rises with decreasing density to the zero point and place of sudden change. This conditions density, valence, and those regularly increasing relations

[1] *Loc. cit.*, p. 160.

which are not reversed or confused by the greater density of the lower semicircle.

1. *The Odd and Even Series of Mendeléeff—Magnetism.*—The elements to the right of the median plane upon the five larger circles and upon the whole first or carbon octave circle form the even groups of Mendeléeff. As determined by Carnalley, these elements are for the most part paramagnetic (except zirconium). The elements to the left on the four large circles and upon the whole of the second or silicon circle and hydrogen form the odd groups of Mendeléeff. They are diamagnetic. It is remarkable with what fidelity this relation is expressed by the two curious curves in Fig. IV, which start with nebulium; one passes through hydrogen and the silicon circle and continues beneath the left-hand half of the four large circles to indicate that they all are odd and diamagnetic, while the second curve is the exact counterpart of the first in position and meaning. They cut each other in helium and neon, thus indicating that the inert gases are nonmagnetic and in an odd-even series.

2. *Organometallic Compounds.*—The elements of the half-octave, the octaves and on to calcium on the first double octave form organometallic compounds; then for the remainder of the elements those on the left of the line *A A* in Fig. IV do the same, while those on the right do not enter into organic compounds.[1]

The law is a direct function of the law of condensation described above.

Passing longitudinally along the helix the condensation does not become so great as to inhibit the formation of organic compounds until the first double octave is reached. Then the transverse condensation comes into play and thenceforward, where it reinforces the increasing longitudinal condensation, there are no organic compounds.

As we go down the first double octave the increasing transverse condensation prevents the formation of organic compounds, after calcium is passed, until the iron group is reached;

[1] I am indebted to Dr. Charles A. Rouiller for the accurate statement of this rule.

thereafter the increasing dilatation along the upward branch of the curve permits their formation, and this rule holds for the rest of the helix.

3. Natural Oxides and Sulphides.—Single and double oxides are most common for the elements on the right-hand downward curves of condensation, single and double sulphides for those on the left-hand upward curve of dilatation. Of elements on the meridian, those in the middle form both, those at the ends neither. See Fig. IV.

4. Reducibility, Native Occurrence.—If a line *B B* (Fig. IV) be drawn just to the right of the meridian and passing through the center so as to leave carbon on the left and silicon on the right, those on the right side are of difficult reducibility, those on the left are easily reduced.

The easily reducible elements on the left naturally often occur native. Those on the right rarely occur native. Platinum is an exception.

5. Atomic Volumes and the Completion of the Atomic Volume Diagram (see Figs. I and V).—Lothar Meyer's diagram of atomic volumes is reproduced upon Fig. I.

It has been prolonged as suggested by Benedict,[1] and carried back to its origin in accordance with the calculations given below. A break has been left in it at a point where there are no recorded observations for a probable upward bend at the place of the next alkali beyond caesium.

This diagram is formed by plotting the atomic volumes (obtained by dividing the atomic weight by the density) as ordinates, and the atomic weights as abscissas. It expresses mainly a transverse function, and in the longitudinal direction distinguishes only the long and the short groups, the double octaves and the octaves.

This is shown clearly by the accompanying table (p. 185), which is formed of the quotients obtained by dividing the atomic volume of each element by the atomic volume of the element immediately above it in the same series, as given in Meyer's table. Thus the atomic volume of sodium divided by that of lithium is equal to 2, and so on.

[1] Z. anorg. Chem., **3**, 40.

Since the elements from rhodium to antimony have practically the same atomic volumes as those in the lower row from osmium to bismuth, I have assumed that the intervening unknown atomic volumes would also be the same.

It is interesting that these ratio numbers range closely about unity in the double octaves, showing that there is no longitudinal variation within these four circles.

They grade from 1 to 2 in passing from the double octaves to the octaves, and range about two in the octaves, with a distinct maximum at the bottom of the curve at carbon.

It is therefore possible to extrapolate quotients for the elements in the half-octave, as is done in the table (numbers in brackets). An inspection of the table will show that as the quotient under chlorine is 1.1 and that under fluorine is 2, that under protofluorine may be assumed to be 3.

From this ratio number the atomic volume of protofluorine can be calculated as follows:

$$\frac{At.\ vol.\ of\ F}{At.\ vol.\ of\ Proto\ F} = 3.$$

$$At.\ vol.\ of\ Proto\ F = \frac{At.\ vol.\ of\ F}{3} = \frac{13}{3} = 4^{1}/_{3}.$$

In the same way the probable atomic volumes of hydrogen and nebulium are calculated and the three numbers are placed against their respective elements. A more forced extrapolation is entered on the table for the atomic volumes of the inert gases by taking the atomic volume of neon to be proportionate to those of magnesium and sodium and the quotients above the inert gases proportionate, respectively, to those on the right. From the atomic volume of neon these quotients give the atomic volume of the other inert gases. This result has a value not for the exact numbers which are obtained but to show the great probability that these values are higher than those of the adjacent alkalies and that the culminations of the curves in Meyer's diagram are at the inert gases and not at the alkalies.

With these numbers the atomic volume curve in Fig. V has been drawn.

The right-hand loop is identical with the Meyer diagram

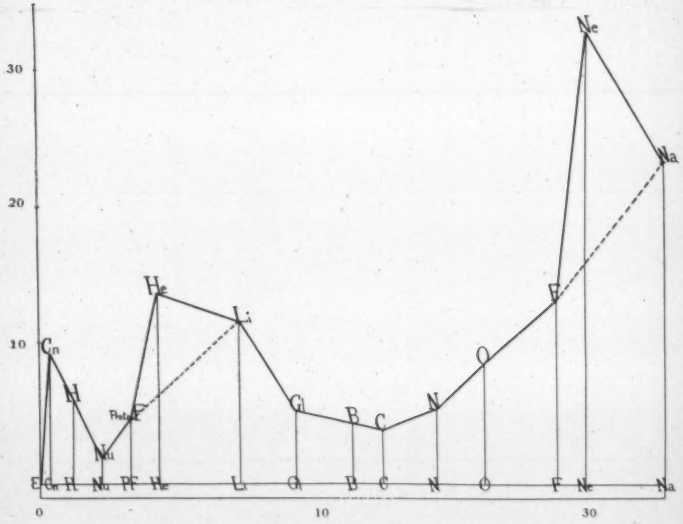

FIG. V.—The atomic-volume curve continued back to the origin and drawn with its culminations in the inert gases. The Li-Na curve continued along the dotted line is the first loop of Meyer's curve. The other parts are calculated from the data given on page 183.

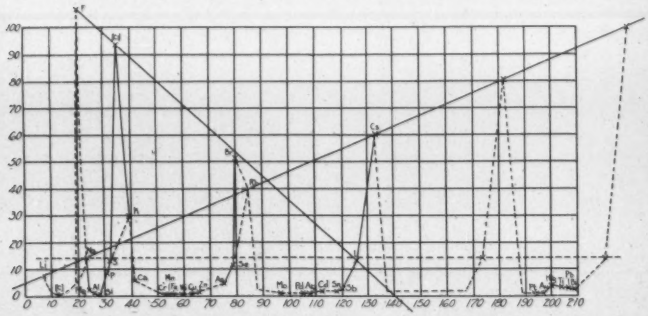

FIG. VI.—The atomic weight-compressibility curve of T. W. Richards altered to show the possible position of the halogens in solid form and to extrapolate alkalis beyond caesium (see page 186).

The line Br-Cl shows the probable great compressibility of fluorine in gaseous form and an impossible negative compressibility of halogens beyond iodine. The horizontal line of heavy dashes passing through I shows the probable position of the halogens (if they could be measured in solid form) below their present one on the chart.

Atomic Volume Quotients.

Cn(13)	H(5.7)	Nu (1.3)														Proto F (4.3)	
(1.5)	(2.1)	(3.8)															(3)
He(19)	Li	Gl	B	C											N	O	F
(1.7)	2	2.8	2.7		3.2										2.7	2	2
Ne(33)	Na 23.7	Mg 13.9	Al	Si											P	S	Cl
(2)	1.9	1.8	1.6	1.1											1	1.1	1.1
Ar(66)	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	Ge	As	Se	Br
(1.2)	1.?	1.3	1.5	1.2	1.3	1.3		1.2	1.2	1.3	1.4	1.4	1.3		1.4	1.2	1.1
Kr(78)	Rb	Sr	Y	Zr	Cb	Mo		Rh	Ru	Pd	Ag	Cd	In	Sn	Sb	Te	I
(1.5)	1.3	1	1	1				1	1	1	1	1	1.1	1.1	1.2		
Xe(116)	Cs	Ba	La	Ce	Pr	Nd		Sm	Eu	Gd	Tb	Ho	Er	Tm	Yb		
				1				1	1	1	1	1	1.1	1.1	1.2		
					Ta	W		Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	ABC
						1.3											
Ra Em		Ra	Io	Th	Ac	Ur											

if we follow down the dotted line from sodium. The newly calculated lithium-hydrogen loop is exactly symmetrical with this. The calculated value 13 is given to coronium and it finds its place as a final culmination in harmony with the preceding culminations of the inert gases and from coronium the line goes down to the origin at the ether.

The atomic-volume curve of Meyer, which omitted the inert gases, had its culminations in the alkalies. The above construction shows that these culminations are most probably in the inert gases. This would signify that the atomic volumes of the inert gases, if obtained in terms comparable with those of the other elements, would be much greater than those of the alkalies and thus the density much less. This makes the atomic-volume diagram harmonize exactly with the helix and gives a considerable value to the numbers used above.

We may further calculate the possible density of the three elements in the solid form, since, if $(at.\ vol.) = (at.\ wt.)/(density)$, then $d = (at.\ wt.)/(at.\ vol.)$. We obtain for coronium $d = 0.3/13 = 0.023$, for hydrogen $d = 1/5.7 = 0.16$, for nebulium $d = 2/1.3 = 1.5$, for protofluorine $d = 0.7$.

This makes the densities of the half-octant agree with those of the other circles in increasing downward to a maximum.

6. Compressibility (Figs. IV and VI).—The compressibility curve of Professor Richards,[1] in large part, agrees closely with the helix and in part diverges from it strongly. A very simple and probable assumption concerning chlorine and bromine would bring it into exact accordance with the helix, *viz.*, that their compressibility *in solid form* would be much less than that given in the table. To show the plausibility of this assumption I have drawn a line through chlorine, bromine, and iodine on the figure, and obtained therefrom an exaggerated compressibility for fluorine (which I have drawn on the figure with dashes longer than those used on the original) and an impossible negative compressibility for possible halogens beyond iodine.

[1] The Compressibility of the Elements and Their Periodic Relations. T. W. Richards: Pub. Carnegie Inst., 1907.

I have then drawn a second nearly horizontal line (in long dashes) through iodine to fix the probable position of the other halogens in solid form. As iodine is far below caesium we may believe bromine would be far below rhodium, chlorine far below potassium, fluorine below sodium, and protofluorine below lithium.

This harmonizes perfectly with the position of the line of the halogens in Fig. IX parallel with the vertical diameter, near to and equidistant from the line of least compression.

I have therefore drawn a dotted line from potassium to a point just above sulphur at the new position of chlorine to complete the second loop, and from rubidium to the new position of bromine, just above selenium, to complete the third loop. I have then drawn a third line through the alkalies and extrapolated two alkalies beyond caesium, and placed the emended graph upon Fig. I.

7. *The Gas Area* (*Figs. II and IX*).—As exhibiting a maximum of volatility, the gases occupy an irregular area in the center of the low-fusing semicircle. It is very peculiar that, as indicated by the chain in Fig. II, the area is symmetrical to the equator in the double octaves and to the ecliptic in the octaves.

The laws of condensation described in Section I explain the area of the helix within which the elements are gaseous at normal temperature. The hydrogen circle contains elements of so small density that they are permanent gases. In the second circle the passage from helium to lithium involves sufficient condensation to compel the solid nonvolatile condition which continues through carbon. Turning upward on the curve, the dilatation is sufficient to immediately cause the change to gas at nitrogen. This continues upward through that half-circle, but passing the zero point at neon, the curve sinks into the solid series immediately below the gas area, and continues in the region of solid elements to silicon. Turning upwards from silicon, the gas boundary is seen to just graze the highly volatile elements phosphorus and sulphur, and to just cut through the liquid bromine in a very significant way.

We may compare the helix to a slanting log sunk into the water. The first coil, containing hydrogen, passes around the log without touching the water and is wholly gaseous. The second passes into the water between helium and lithium, and becomes solid but quickly emerges on the other side beyond nitrogen, and is gaseous during most of the circuit. The next downward turn passes quickly into the water at sodium, and is under the surface through three-quarters of the turn. The succeeding turns emerge only far enough to make place for a single gas, and not far beyond the radium emanation we may believe that the whole circuit would be solid if conditions favored its formation.

If the reason for the formation of gases on the upper side of each curve is found in the law of transverse condensation, the reason for the diminution of the gas area in passing from curve to curve in the direction of motion is due to the law of longitudinal condensation. In Fig. II I have indicated this by the slanting position of the helix which dips to the right at such an angle that the line of boundary of the gas area (represented by a chain) passes across it horizontally like a contour line. Above it is drawn the graph expressing the law of longitudinal compression and of increasing density and the model is so placed as to make the chain horizontal to symbolize the amount of depression due to this increased density.

It is very curious and interesting, however, that while this contour relation holds with regard to the large curves and the gas boundary is parallel here to the equator of the figure, in the small circles this boundary sinks with an angle of 45° and places itself parallel to the ecliptic of fusion, (See Fig. VIII) bounding the volatile semicircle. Thus the gas area sags to include the two gases oxygen and nitrogen, which are found to be abnormal also in their density (see page 201) and in their atomic heat, as shown in the section below.

8. The Rock Area.—In Fig. IX the apex of the gas area which enfolds the elements of the nebulae and the elements of life tapers upward and forward like a flame, forming the center of the volatile semicircle. A similar figure,

pointing downwards and backwards, forms the center of the high fusing semicircle and includes the rock-making elements, silicon, aluminium, magnesium, sodium, potassium, calcium and iron. This forms the lithosphere and points downward and backward toward the centrospere, where are the heavy magnetic triads.

Inspect this figure and see how suggestive is the position of every element in the little group.

Potassium stands at its apex, suggesting the lightest feldspar and the lightest of the rocks, as pegmatite.

Next below is sodium and beside it and a little below is calcium, suggesting the soda-lime feldspars, the intermediate rocks and the Howardites among the meteorites. Thus far we are in the salic region.

Far below is magnesium, suggesting the heavy olivine, the ultrabasic rocks and the Chondrites among the meteorites.

Much farther below are iron, cobalt, nickel, suggesting the sesquioxide segregations, the basic border-rocks, and the Pallasites and Siderites among the meteorites. This is the femic region.

On one side of the middle of this row of low-valence bases the single trivalent base aluminium links the whole with the single tetravalent acid-maker silicon at the center.

9. *The Stability of the Oxides.*—When subjected to rising temperatures the stability of the oxides of the elements varies according to two laws:

(*a*) When the elements are followed radially the stability decreases inwardly (as from caesium to lithium) in the first semicircle, and decreases outwardly (as from fluorine to iodine) in the second semicircle.

(*b*) When they are followed along the line of the helix (as from potassium to titanium) the stability decreases through the first semicircle (as rubidium to molybdenum), increases through the third octant (as copper to germanium) and decreases through the fourth octant.[1] Compare electropotential relations (p. 190).

[1] A. E. Garrett: The Periodic Law (1909), p. 193.

SECTION III.—EQUATORIAL RELATIONS (SEE FIG. VII).

The diametral plane is prepotent, and where the relations are also strongly influenced by the equator they are mostly divided in quadrants. The main equatorial contrast is that the upper half of the double octaves is strictly homologous with the whole of the single octaves, and shares with them the simple valence, the marked changes at the zero point, and the marked contrast on either side of it. The lower half of the double octaves has complex valence, and culminates without strong contrasts in the triads, in the midst of the heavy, highly-colored, and magnetic metals. Above, along the axis, in a region of ideal expansion, are strung the inert gases, without elective affinity or allotropic forms—strict unitarians. Below, in a region of greatest compression and narrowness, are strung the four triad groups, with valence ranging from one to eight—true trinitarians, the varying valence symbolic of sectarian tendency.

The equator thus divides the whole into a northern hemisphere of maximum compressibility having elasticity, high electropotential, and all the elements of elevation, evolution, and civilization, and a southern hemisphere of minimum compressibility, comparatively inert and undifferentiated, containing the heavy metals and the most complex molecules. The upper hemisphere is in the region of simplest spectra, the lower in that of the most complex spectra, and in many series the lines at the blue end of the spectrum appear in the elements at the top, and there is a gradual passage downward toward the red end of the spectrum.

SECTION IV.—THE QUADRANTAL RELATIONS.

1. *Electropotential Relations* (*Fig. VII*).—Abegg's table[1] of the electropotentials finds very clear expression upon the diagram by decreasing plus and minus signs. It is in general a quadrantal arrangement. The strong electropositive capacity of the alkalies decreases regularly to zero, at the bottom of the first quadrant. The strong electronegative capacity of the halogens decreases regularly to zero at the bottom of the fourth quadrant. Here at the equator the sign changes, and

[1] Z. anorg. Chem., **39**, 330 (1904).

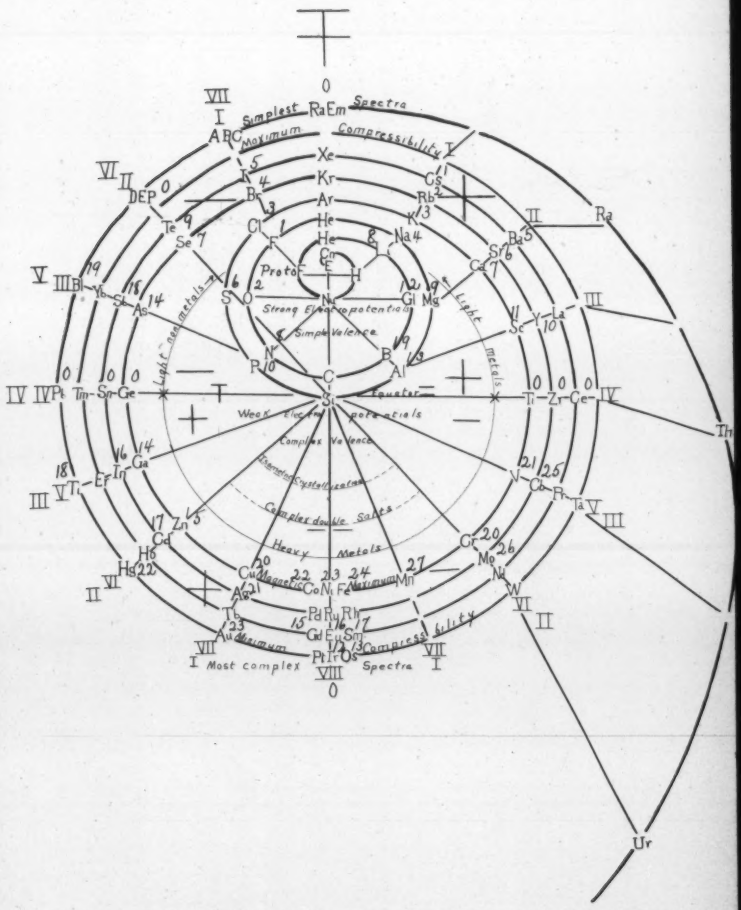

FIG. VII.—Equatorial and Quadrantal Relations. Values of the Electropotentials of the Elements in Detail. The printed numbers represent the order of these values, beginning with the highest. The written numbers give the group or longitudinal atomic weight differences. See page 190.

the value becomes plus in the third quadrant and minus again in the second, but in each case with lessened power, the electronegative force decreasing to a minimum near molybdenum, the electropositive to a minimum between mercury and silver.

The details of this relation are also brought out clearly by the numbers placed against the different elements. A curious contrast is brought out, in that the electronegative capacity decreases in the direction of the axis of the helix, while the electropositive capacity decreases in the reverse direction. The negative decrease goes outward along the halogen series regularly, but springs back to take in oxygen. It then starts along the oxygen series regularly but springs back to take in nitrogen. It then starts along the phosphorus-arsenic series regularly, but springs back to platinum, iridium, osmium and arsenic, and thenceforward there is no regularity.

The positive decrease, on the other hand, starts with caesium and goes regularly backward to sodium. It then starts back to take in the barium series before taking in the rest of the alkali row, and so on. This is similar to the order of stability of the oxides (p. 189).

This finds a possible explanation in that the relation is a function of the condensation. The electronegative force *decreases* along each horizontal series (as the halogens) with increasing longitudinal condensation, and decreases down each circle with increasing transverse condensation. The electropositive force *increases* along each horizontal series (as the alkalies) with increasing longitudinal condensation. It is a question in each case whether the longitudinal or transverse condensation shall be the more effective.

The electronegative maximum is at fluorine at the point of least condensation. The line down to oxygen is a direction of increasing transverse condensation, and the line along the halogens is a direction of increasing longitudinal condensation. The former prevails; oxygen comes in second, and then the effective increment of condensation follows along the halogens and the sulphur series, but before tellurium is reached the transverse increment of condensation raises nitro-

gen to a condensation greater than tellurium, and so nitrogen precedes tellurium.

After phosphorus, the next value jumps to the most condensed portion of the opposite quadrant—the platinum group—and then oscillates between these quadrants with a curious rhythm to end near molybdenum.

The plus series is the counterpart of the minus one, beginning at the most condensed end of the alkali group and working backward to lithium. The curious torsional arrangement of these potentials suggests a connection with the dia- and paramagnetic relation.

It is even more difficult to understand the passage from the electronegative halogen line through the inert gases to the electropositive alkali line. It is symbolized rather than made intelligible by the statement that it is a passing through zero with change of sign.

This may find its physical explanation in the idea that on each ascending arc the maximum of dilatation is reached or approached at the line of the inert gases, and this is also near the maximum of mobility and has minimum valence. Here the addition of the smallest mass equal to about a hydrogen atom—the equivalent of a single interspace or interweight—to each halogen (see Fig. X and Sec. 5, p. 202) brings about an exceptional equilibrium in the corresponding inert gas, wherein there are no free electrons, and a condition like that of a haloid compoundis reached, and this is so stable that it requires the addition of the maximum mass, equal to a helium atom or more, to break the "dead center" as we say in mechanics, or to pass the zero point as we say in mathematics, and give rise to an atom of such great mobility that a complete rearrangement of the rings occur sand an atom with one free electron and a maximum positive electropotential capacity is formed in place of one lacking one electron and with the greatest electronegative character.

It is, however, to be noted that at first in the octave the minimum density is reached at the culmination in the inert gases; in the double octaves, beyond the culmination at the alkali line. See Fig. XI.

It is further interesting that each halogen approaches the zero point with a less electronegative capacity than its predecessor and emerges as an alkali with a greater electropositive capacity than its predecessor.

In comparing the inert gas with a halogen compound, I have followed an unpublished suggestion of my former pupil and good friend, Professor C. S. Palmer, who has done so much to increase our knowledge of the periodic law, that the inert gases are inert, not because they are without chemical affinity, but because they in a sense combine the electropositive and electronegative character, and so I have put ± above them, with the large size appropriate to this position.

2. Melting Points of the Haloids.—The mean melting-point curves of the normal chlorides, bromides, and iodides of the elements[1] take the same quadrantal arrangement as the electrical potential.

From a maximum in the alkalies the melting point decreases in the octaves and rises again to the halogens. In the double octaves the decrease in the first quadrant is followed by an increase in the second to a subordinate maximum in the copper series, followed in its turn by a decrease in the third quadrant, and a sharp increase to the halogens in the fourth.

The graph is reproduced on Fig. I. The dotted line is introduced only to connect the significant parts of the same.

3. The Shifting of the Colors of the Spectra.—The elements of the different subgroups or radial series, as the alkalies, have spectra which are similar in the number of bright lines visible and the groups into which those lines may be divided.

Their characteristic or homologous lines change regularly in color, in passing outwardly in radial direction, and this change is toward the red end of the spectrum in the first and third quadrants, and toward the violet end, so far as observed, in the second and fourth quadrants.[2]

4. Crystallography (Fig. VII).—The ecliptic and its vertical divides the helix into a lower, upper, and two lateral quadrants. In the lower quadrant the cubic system prevails,

[1] Carnelley: The Periodic Law. Chem. News, **53**, 171.
[2] A. E. Garrett: The Periodic Law (1909), p. 171.

though some few elements show also the analogous rhombohedral system.

In the two lateral quadrants the tetragonal, rhombic and monoclinic systems prevail. Indium is cubic, and vanadium, magnesium, bismuth and antimony are hexagonal, generally as an allotropic form.

In the upper quadrant only the alkalies are known in crystal form and then are quadratic, except lithium, which is cubic. There is thus the greatest symmetry connected with the greatest condensation.

5. *The Law of Dulong and Petit* (*Fig. IX*).—The failure of the elements to obey the law of common atomic heat stands in distinct relation to the tendency to form gases, but the area containing the abnormal elements is almost symmetrical to the meridian. It coincides with the upper part of the gas area, and the right-hand boundary of the latter is continued downward to include glucinum, beryllium, carbon, silicon, phosphorus and sulphur when it joins again the left-hand boundary of the gas area. It requires thus a little greater condensation to establish the law of common atomic heat than to introduce the solid form.

SECTION V.—THE ECLIPTIC RELATIONS (FIG. VIII).

1. *Fusibility and Volatility.*—A diameter bisects the first and third quadrants like an ecliptic, having on one side the high-fusing metals and on the other the volatile and low-fusing elements. The maximum fusing point lies between manganese and chromium, and the high-fusing area extends to the beginning of volatility in the zinc series. Thus this diameter has, curiously, the liquid mercury at one end and the luminous radium at the other. It is further remarkable that this diameter of the large circle cuts off a sectant from the small circle which separates the three high-fusing element groups from the five low-fusing, volatile or gaseous groups. This is slightly misleading, since in a true figure the small (octant) circle is raised above the fusion diameter. This sector dividing the small circle remains, however, strictly parallel to the fusion diameter when the figure is correctly drawn (see Fig. III), so

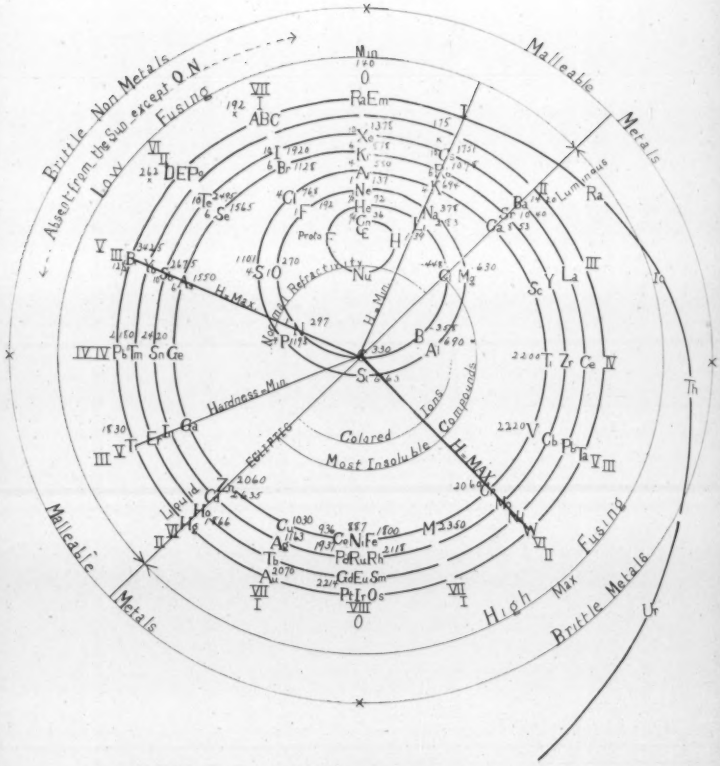

FIG. VIII.—Ecliptic Relations. Refractivity in Detail.

The large number on the right is the coefficient of refractivity. The small one at the left represents the factor to be multiplied into the constant at the border to obtain this refractivity.

For refractivity see page 177; for colored ions, page 195; for malleability, page 196; for insoluble compounds, page 195; for fusibility, page 194; for hardness, page 196.

that the suggested symmetry is not impaired. It was by pure chance that the figure was drawn so as to make these two lines coincide.

2. *Solubility.*—The ecliptic also separates the elements forming mostly insoluble compounds, on the lower or heavy side, from those forming mostly soluble compounds, on the upper volatile side (Carnelley).

3. *Elements Wanting in the Sun.*—Most peculiar of all the ecliptic relations is that the middle quadrant of the volatile semicircle contains elements which are wanting in the sun, except oxygen and nitrogen, the atmospheric elements, in the center. Have they been volatilized therefrom, or is it only a defect of spectrum analysis?

4. *Colored Ions.*—The lower three-quarters of the high-fusing semicircle are occupied by the colored-ion makers, and this is essentially an ecliptic relation, though this relation is first established an interspace below the light malleable metals.[1]

5. *Refractivity.*—The upper three-quarters of the low-fusing semicircle are occupied by the transparent refrangible elements which also obey the law of longitudinal periodicity, as described in Section IV, 2, p. 177.

That this area is the "Spiegelbild" of the colored-ion area is significant, since the transparency of the volatile elements which make refraction possible is the opposite, as a color producer, of the strong absorption of the colored metals, and the two exclude each other.

As the elements obey the law of the octave in their refractive capacity in the region of greatest dilatation, so in the region of greatest condensation, absorption takes the place of refraction and colored ions are produced.

The line representing the distribution of colored ions is dotted at either end to cover the transitional elements which produce partly colored ions and partly uncolored ones. This line divides the elements exactly except that thallium and bismuth sometimes produce colored ions. After the above result was worked out the diagram—the arbitrary diagram he calls it—of Rudorf[2] was found.

[1] Carey Lea: Chem. News, **73**, 203 (1896).

[2] George Rudorf: Periodic Classification (1900), p. 119.

A comparison shows the greater elegance of the above arrangement, especially in bringing out the relation of colored ions to refractivity.

6. Hardness (*Fig. VIII*).—The hardness of the elements is distributed as a peculiar variant of the ecliptic relation.

Platting the table of Von Rydburg,[1] the maximum hardness 10 comes at the ideal center in carbon. The line of maximum hardness is the radius through chromium at right angles to the ecliptic.

At the center this line branches symmetrically and two minima pass along the radii through gallium and lithium, and a subordinate maximum, instead of going straight on through selenium, passes one point to the left through arsenic. To avoid confusion this is shown on the diagram by lines and not by introducing the numbers. Only the averages are indicated by the relative size of the type.

The law is very clearly realized and this illustrates a useful method of expressing a complex relation by means of the helix.

7. Valence.—Valence is a purely transverse function; that is, in passing along the alkalies the valence cannot be said to change in any way from unity; and so in the other groups.

The principal valence is a purely meridional function, increasing from O at the top to VIII at the bottom of the meridian either way.

The whole valence has an ecliptic quadrantal relation. It is simply O to IV in the first quadrants; complex O to IV and VIII to IV in the third. In the second and fourth quadrants it is IV to O and IV to VIII.

This is best shown on Fig. III.

8. Ductility (*Fig. VIII*).—The meridian and equator divide the helix into quadrants symmetrical to the ecliptic. The first and third quadrants contain the malleable metals, the second contains the brittle metals, and the opposite fourth quadrant contains the brittle nonmetals.

9. The Quadrilateral of Life (*Fig. IX*).—At the base of the gas area is a strong quadrilateral, CHON, a symbol used many

[1] Landolt-Börnstein: Physikalisch-Chemische Tabellen, 1905.

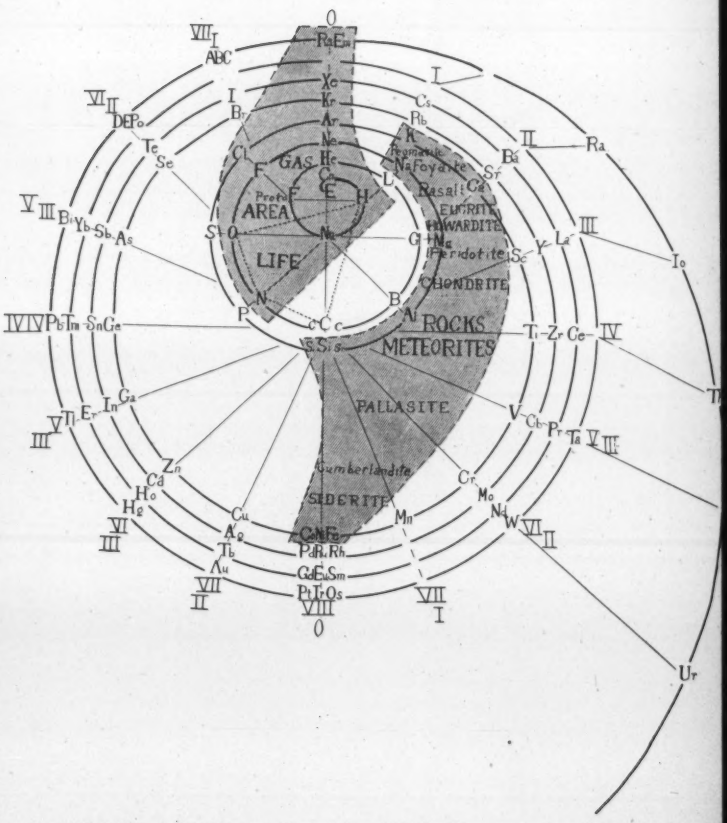

FIG. IX.—Allied relations of partial or complex symmetry which do not come into the preceding categories. They are described in the section with which they are most nearly related: The gas and rock areas as diametral on page 187; the law of Dulong and Petit as equatorial on page 194; and the quadrilateral of life as ecliptic on page 196.

years ago by the fine zoologist, Henry James-Clark, to signify the life-bearing elements, or protoplasm. Of this quadrilateral ON represents the atmosphere, OH the ocean, OC carbonic acid and CH the hydrocarbons; while the quadrilateral is fringed by all the subordinate elements of protoplasm, and has Na and Cl, the characteristic compound of the salt water, the common menstruum[1] of life, in a most symmetrical position directly above.

SECTION VII.—THE LAW OF THE OCTAVE.

In a sense the law of the octave holds not only transversely but longitudinally. We have already expounded and expanded Newland's law of the octave, as it applies to the elements transversely (Chapter II, p. 170). Each inert gas is the first note in a new octave, each alkali the second—the half-octave is followed by two octaves, by four double octaves and one quadruple octave.

Proceeding in the other direction, or longitudinally, and going out from the center in each series, as the alkalies, the elements, barring in some cases polymerization and the gaseous condition, have been found to increase in density according to Goldschmidt's law of complication, which is also the law of the harmony of the octave in music. Many other harmonic relations which depend more or less upon the density follow in varying degree the same law, as shown in the following table:

Goldschmidt's Law	0	1/3	1/2	2/3	1	3/2	2	3	∞
Condensation (see p. 174)	0	1/3	1/2	2/3	1	3/2	2	3	
Supposed atomic vibration of Batschinski (see p. 178)		1/6	1/2	2/3	1	4/3	5/3	2	7/3
Refractivity		1/16	1/8	1/4	1	3/2	5/3	2	

These are first crude approximations, and vary where the data are uncertain. They will surely approach more nearly to each other and to Goldschmidt's law of complication with further investigation.

CHAPTER IV.

1. On the Exact Position of the Elements on the Helix.—The

[1] R. Quintan: L'Eau de Mer Milieu Organique, Paris, 1904 A. C. Lane: Science, **26**, 129 (1907).

horizontal line through hydrogen (see Fig. III) cuts off one-fourth of the second circle in either direction, *Cn H*, which equals unity. The elements occupying positions on this circle may be thought to be exactly fixed in position, and to be very simple, as indicated by low valence, combining weight, density, and by simple spectra.

The continuation of this line cuts off a distance almost equal to 2 on the octave curve, namely, *Cn Li*, which equals 41° 25′; while 45° on this circle equals 2. In the same way this line cuts off on the double octave curve a length of 23° 33′, *Cn K*, while 22° 30′ equals 3. On the last curve the line cuts off *Cn O*, which equals 14° 20′, while 11° 15′ equals 4. This symbolizes the fact that on the larger circles the position of the complex elements is a small area rather than a point, as seen by the slight lack of agreement with the nearest diameters in the diagram where the line cuts each of the larger circles.

Even with this latitude, it is found that when the elements are put in their true relative positions in accordance with the differences of their atomic weights, as in the atomic weight helix described below, the agreement with their ideal positions is much less perfect than might have been expected, and curious and unexpected symmetries come to light (see Fig. X).

It is further found that the elements can be nearly as well placed on the curve by using the successive differences of the densities, as in the density helix below (see Fig. XI), and that the inequalities of the two curves largely counterbalance each other, the first being as much too advanced as the other is retarded. So that a table made by taking the average position indicated by the atomic weight and the density differences, as in the third helix below, brings the elements much nearer the true position (see Fig. XII).

It is then inferred that the distance on the last curve by which each element is separated from its ideal position, taken with opposite sign, would represent the value of the remaining functions (perhaps principally valence) which influence the position of the elements.

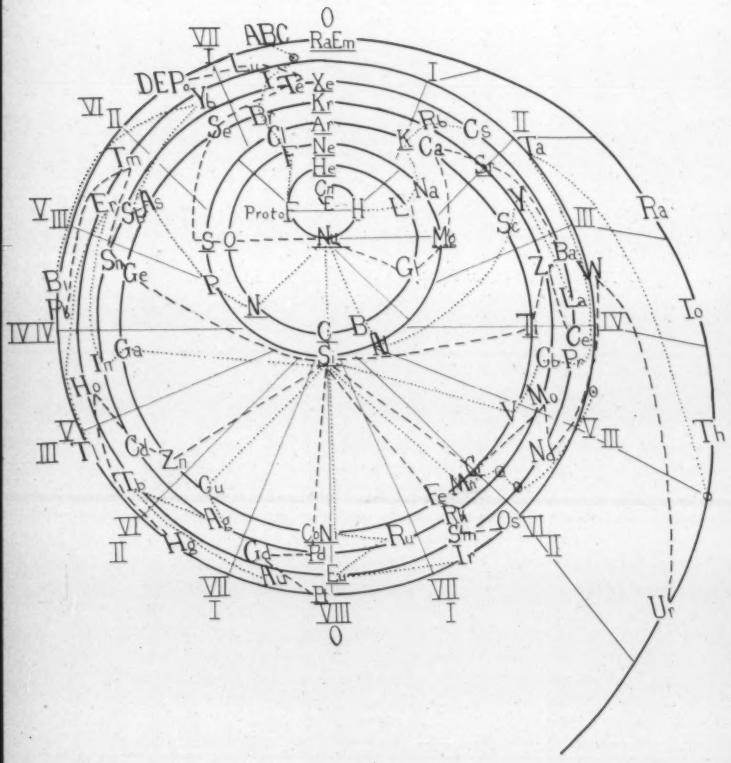

FIG. X.—The Atomic Weight Helix.

The elements are placed upon the helix, in accordance with the real differences between the atomic weights. See page 199.

This brings into clear light the relative importance of valence, atomic weight, density, and the ideal "position." The atomic weights have had a primary value in placing the elements in that natural order, which has brought out their periodic or harmonic relations, and the suggestion of a "position" of ideal symmetry. It has had something of the value of a scaffolding to the completed building.

The density and valence have aided in breaking the curve into its harmonic periods.

Measurement by the atomic weight is something like measurement from the absolute zero, or from the beginning of a journey; measurement of density along the separate groups is like measuring from a fixed zero or from the beginning of each day's journey.

This measuring may be in terms of atomic weight, density, or other harmonic relations, but in the formation of the regular "series" in the periodic table it has been assumed that valence and the ideal "position" number were identical.

Will it be possible to find such values of the valence and other functions as, combined with the values of the above diagram, Fig. XII, will bring the elements into their ideal positions?

2. *The Atomic Weight Helix.*—In Fig. X the elements are put in their true places in accordance with the real interspaces between them found by subtracting each atomic weight from the following one.

All elements which retain the ideal position are underlined.

There is a certain justification for this construction in the fact that when the helix is thus formed the heavy elements at the bottom of the meridian and many at the ends of the horizontal diameter also retain their ideal position.

Since the elements are placed for convenience on circles of gradually increasing size, which yet represent nearly the same advance in atomic weight, the length of each circle was obtained by subtracting the atomic weight of the inert gas at its beginning from that at its end, and with this as a denominator and each interspace as a numerator the proper fraction of 360° was obtained and protracted upon the proper

circle. A dotted line connects the elements of each series and shows how far they depart from the ideal position.[1]

The elements are assumed to stand symmetrically in the small hydrogen circle. In the octaves the interspaces are the normal number, 2 or either 1 or 3, and the elements thus occupy either the ideal or the intermediate position.

The elements of the potassium or principal circle are more nearly in place than those of any other of the double octaves. There is developed a perfect meridional symmetry. Cobalt and nickel are nearly in the ideal position together and yet face opposite ways. With curious alternating symmetry a loop goes out in the second circle to ruthenium on the right, and its counterpart goes out to gadolinium in the third circle and to the left.

An inclined N is thus formed, which on the right reaches a minimum expression in the manganese and vanadium lines and rises to a maximum in the calcium line and then decreases slightly. The lines assume inclined M-shapes when, with the chromium line, the radium-uranium elements join the series.

In the second semicircle the M-shaped figure is the counterpart of the preceding and quickly reaches a maximum and in the last line but one fails to return upon itself, thus carrying tellurium far beyond the vertical haloid line, which is abnormally flattened.

The point of first interest is that in the midst of much apparent irregularity, carbon and silicon and one element in each triad occupy exactly the end of the vertical diameter opposite the inert gases, so that all irregularities are compensated within each semicircle, and a fresh start is taken. Thus the irregularities of the descending and of the ascending curve have each its own law, as was seen in the deduction of the laws of condensation.

Unlike all the other groups, the halogens fluorine and chlorine are crowded beyond their proper symmetry position to a point close up to the line of the inert gases, from which they are separated by only a unit interspace, and this and the axial position of the inert gases are the only points in which the octaves and the larger curves show similarity. (See either side of the

[1] Unknown elements are placed halfway between their neighbors.

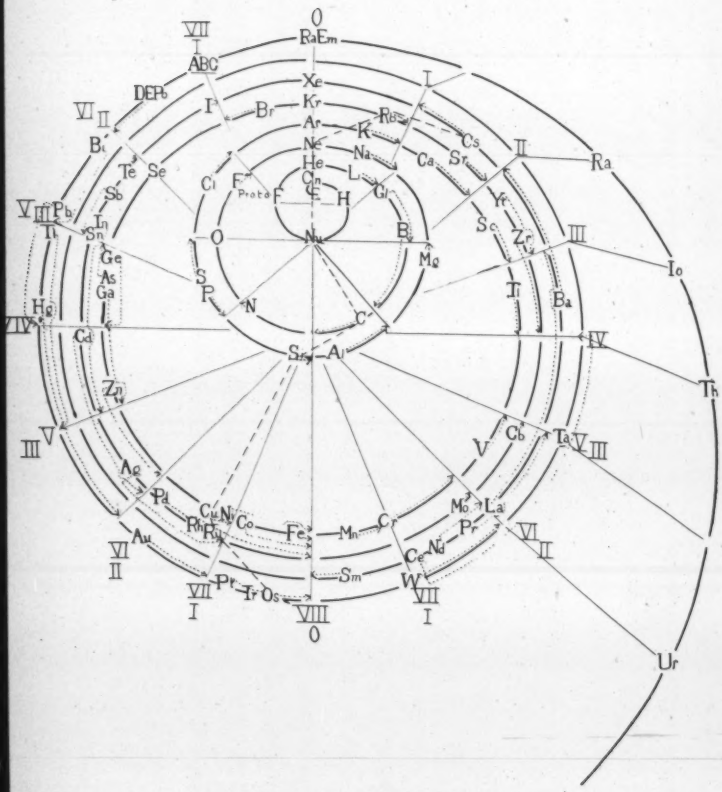

FIG. XI.—The Density Helix.

The elements are put on the helix in accordance with the real differences between the densities and brought into their ideal position by a dotted line (see Chap. IV, page 201).

The upper part of the line of dashes above E is the line of minimum recorded density; the lower part, that of maximum density.

line of the inert gases on Fig. X and the table on page 203).

It is as if all the halogens, moving parallel to each other along their respective circles like a row of runners, had come up to a fixed point, close to the zero line, at the best distance from which to make the jump over this zero line, and as if they had got so much momentum that they landed (like Alice jumping through the looking glass), transformed from most negative acid-makers to most positive alkalies, at points far beyond the line of symmetry, only excepting potassium, the leader of the central circle—the "dominant" of Goldschmidt's law—which landed and halted at the line of symmetry and stands on the circle high above the others, Al-Kali, king of the alkalies.

3. The Density Helix (*Fig. XI*).—The elements are here placed on the helix in accordance with the interspaces between the successive densities, the inert gases furnishing, as before, the origin of measurement.

A single curious adjustment was required. The abnormal gases, nitrogen and oxygen, which cause the gas area in the octaves to sink into parallelism with the ecliptic line (see Fig. II and page 187) require to be multiplied, nitrogen by 3, and oxygen by 3/2, and they are then brought into their ideal positions.[1] With this exception the elements come into an arrangement similar to and hardly less regular than that obtained above with the atomic weights. There are a few overlaps as in the former curve. The alkalies and the halogens are indeed nearer the ideal place. In the first quadrant there is the same sharp bend forward, exaggerated in the case of barium, lanthanum and cerium. An N-shaped figure directed backwards dominates the second quadrant, which is replaced by an advancing N in the case of iron and in the third quadrant this would probably be continued; but as there are no values known for the elements in the third circle, the N is replaced by an advancing V, which flattens into a straight line as it passes into the fourth octant.

It is to be noted that the line of minimum density is on the

[1] This may give a hint as to what the density of these elements would be in the solid form.

axis up to neon, but one period to the right in the line of the alkalies from caesium to potassium, while the line of maximum density shifts by the same amount to the left in the case of copper at the other end of the diameter.

4. The Combined Density-Atomic Weight Helix (*Fig. XII*).—Assigning to each element the average of its values on the preceding diagrams, a curve is produced that approaches the elements in a marked way to their ideal position. The smaller symbols give the ideal, the slanting ones the real position.

It brings out strongly the fact that the values are largely advanced beyond the ideal position in the atomic weight numbers and the opposite in the density numbers.

5. The Persistence of the Unit Interspace between the Halogens and Inert Gases and the Combining Weight of Argon.—The following table, formed by looking down on the helix from above, makes clear the curious interspace relations on either side of the line of inert gases.

The lowest line is hypothetical. In the second to the fourth lines the interspace should be $2 + 2 = 4$. It is $1 + 3 = 4$.

On the fifth to seventh lines it should be $3 + 3 = 6$. In the best measured case, iodine to caesium, it is $1 + 5 = 6$.

In the upper or long circle the interspace should be $4 + 4 = 8$. It is $1 + 7 = 8$, as far as the numbers can be made out in this uncertain region.

The above result is obtained, it will be observed, by changing the atomic weight of argon to 36.

The combining weight of argon is obtained by indirect methods for an element which does not combine, and the determination is much less certain than for chlorine or potassium.

As we obtain the position of neon or xenon by adding 1 to tellurium or iodine, so we should be able to do with argon or krypton. Having done so, we obtain numbers which have the normal interspace relation in the vertical column, about 16 between neon and argon, about 46 between the others.

Lord Kelvin has calculated the size of the atom and found 35.62 for the argon molecule.[1] Ramsay has calculated that if five per cent. of the gas were monatomic it would have an atomic weight 36.

[1] Phil. Mag., [6] 4, 301.

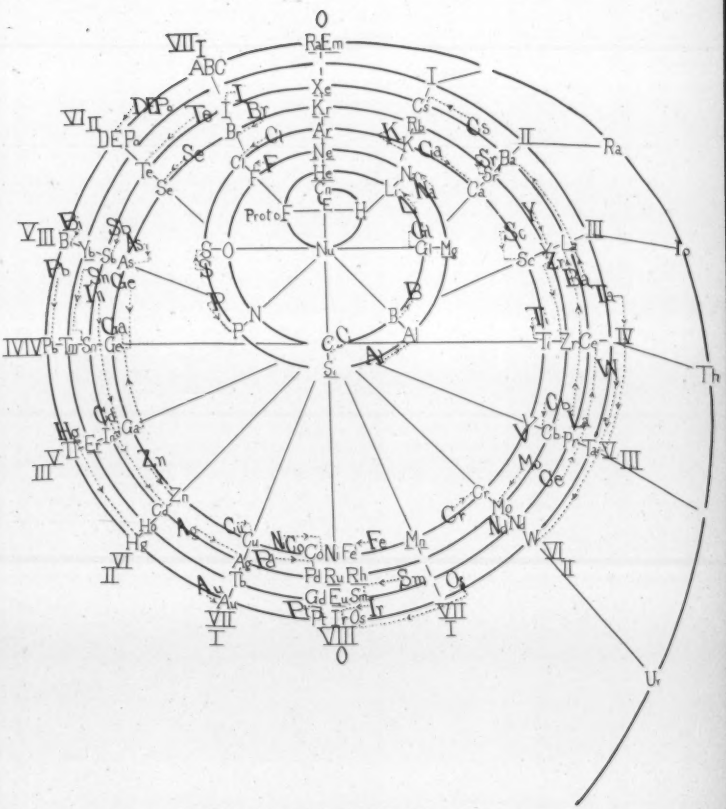

FIG. XII.—The Atomic Weight and Density Helix.

The elements are placed (in larger slanting letters) upon the helix in accordance with the average of their densities and their atomic weights. Those which retain the ideal position are underlined, the others are brought into their proper places by a line of dots.

Halogens with transverse interspaces.	At. wt.	Longitudinal interspaces.	Inert gases with transverse interspaces.	At. wt.	Longitudinal interspaces.	Alkalies with transverse interspaces.	At. wt.
A, B and C emanations	220.0	1.0	Radium emanation	221.0	1.0	(Thorium X)	222.0
45			45			45	
Unknown	175.0	1.0	Unknown	176.0	1.0	Unknown	177.0
48.15			48			44.1	
Iodine	126.85	1.15	Xenon	128.0	4.9	Caesium	132.29
46.89			46.2			47.4	
Bromine	79.96	1.84	Krypton	81.8	3.7	Rubidium	85.5
44.51			45.8			45.35	
Chlorine	35.45	0.55	Argon	36	3.15	Potassium	39.15
16.45			16			16.15	
Fluorine	19.0	1.0	Neon	20.0	3.0	Sodium	23.0
16			16			16	
Protofluorine	3.0	1.0	Helium	4.0	3.0	Lithium	7.0
3			3.7			6	
E	0	0.3	Coronium	0.3	0.7	Hydrogen	1.0

There remains, in connection with the persistence of the unit distance along the whole inert gas series, the fact that the average length of the long circle seems to be near 46 instead of near 48. It seems possible that the interspace before the inert gases which should be 3 is condensed into 1, and that without compensation, thus reducing the whole length from 48 to 46. More weight is probably to be put on the fact that the most accurately determined elements give a number near to 48 (as barium-strontium, strontium-calcium).

CHAPTER VI.

1. Atomic Weight Formulae and Diagrams.—I asked my colleague, Professor T. C. Esty, to consider the formula which would express the curve of the helix, and he assured me that a formula for a disconnected series of five circles would be extremely complex, and would be moreover only useful to deduce just the relations which have already been obtained by observation, as given in the table on page 169.

The ideal relations of the elements as expressed or implied in the complex helix are so harmonic that it is not strange that many have been impelled to search for some equation which would give the atomic weights.

The many empirical equations from which the atomic weight may be approximately deduced seem to depend largely upon the fact that any series of numbers separated by small and varying differences may be represented by many equations which will give the numbers with errors that rarely surpass the difference between the numbers themselves. Thus the latest of these equations,[1] $W = (N + 2)^{1.21}$, where N equals the number representing the position of the given element in the whole list of the elements as arranged in Mendeléeff's table, gives remarkable results, but seems to depend upon the fact that the normal interspaces are two and three in the cases concerned, so that adding two to the position number and increasing it by the small exponent will give generally an approximate result.

[1] J. H. Vincent: On a Numerical Connection between the Atomic Weights. Phil. Mag., [6] **4**, 103.

All these equations seem to derive their value from the fundamental importance of the position number.

Of all these equations and diagrams, that of Johnstone Stoney is the most wonderful and suggestive.[1] It is indeed particularly suggestive that it was apparently originally rejected by the Council of the Royal Society, and published by its author only after it was found to contain the prophecy of the whole helium series.

On inspection the figure shows that if the two inner circles were coiled with half radius the triads and alkalis would be brought each into a single series; and the need of the curious sesquiradii and the assumption of a logarithmic spiral are avoided.

I cannot refrain from calling the attention of organic chemists to the remarkable right- and left-handed spirals of Thomas Carnelley,[2] who did so much to develop the harmonic relations implied in the periodic law.

He prepared a table of the haloid salts of the organic bases, and showed that these bases, when placed in the order of increasing complexity and combining weight, exhibit a remarkable parallelism with the elements in the periodic table. This was remarkable as suggesting the complexity of the elements. He then arranged the series of organic bases and the elements in similar spirals, much like the diagram of Stoney, and came on the peculiar result that the elements form a right-handed and the organic bases a left-handed spiral.

2. *The Direction of the Growth of the Elements.*—The direction of the devolution of the radio-active elements is usually assumed to be backwards along the curve of the helix, and the direction of evolution is usually assumed to have been along the curve in the order of the increasing complexity of the elements, and this assumption underlies the preceding discussion. This is the order in which the molecules of the elements have been built up by the successive addition of electrons according to J. J. Thompson.[3]

It has been argued in a recent important and baffling paper[4]

[1] Phil. Mag., [6] **4**, 411 (1902).

[2] The Periodic Law. Chem. News, **83**, 171.

[3] On the Structure of the Atom. Phil. Mag., [6] **7**, 237.

[4] A. C. and A. E. Jessup: Evolution and Devolution of the Elements. Phil. Mag., [6] **15**, 46.

that evolution was in part radial, and so the elements of each series, as the alkalies, are bound together genetically.

The argument is advanced that, because the nitrogen-bismuth series is wanting in the sun, the whole series has never been developed in the sun, and thus is a series that appears or fails to appear as a unit. Since the spectra of these elements can be detected only with difficulty in the laboratory when metals are present in abundance, the apparent absence of their spectra in the sun cannot be made the basis of any strong argument for the absence[1] of the corresponding elements.

Moreover, the presence of the cyanogen lines would indicate the presence of nitrogen, and the absence of the whole fourth or volatile quadrant except the central elements (see Sec. V, 3, page 195) would connect their absence with their volatility.

Also the order of appearance of the elements, and especially the late appearance of sodium, in the hot stars may better be put among the unexplained phenomena of a difficult subject than as proof of radial evolution.

The argument is advanced that the helium, lithium, glucinum and fluorine series are evolved outwardly in the sense that helium becomes neon, lithium becomes sodium, sodium becomes potassium, and so on. This is called the principle of heredity; that similar elements of like valence should be derived from each other. Thus, for example, barium should be derived from strontium because they are both bivalent and in the same series. This involves the addition of 49.8 in weight to the strontium atom to make barium, and it seems more reasonable to derive it by the small addition of 4.5 from caesium.

Moreover the principal is not carried through consistently, but an unexplained process of "indirect evolution" is introduced, by which the four elements, carbon to fluorine, the ten elements, vanadium to germanium, and many of the heavy metals near copper (indeed, the majority of the elements)

[1] G. F. Becker: Radio-Activity and Cosmogony. Bull. Geo. Soc., **19**, 113.

are derived from each other in the order of increasing atomic weights, as is ordinarily assumed for all the elements.

The marked harmonic relations existing between the elements of the four series mentioned above to which the "law of heredity" applies find a satisfactory explanation if we assume them to have been derived in the order of their atomic weights like the others.

We may say that sodium is like lithium, barium like strontium, because they are the corresponding notes of the next higher octave, and not because of any principle of derivation or heredity between them, just as there is in music a harmonic relation between the A of one octave and the A of all the other octaves, without there being any proof therefrom that these A's have been derived directly the one from the other.

Indeed, the peculiar equations derived in the article, by which the atomic weights of the beryllium series are calculated, will find application equally well on either method of derivation, whether calcium is derived from magnesium by the immediate addition of 31 in weight, or whether this addition has been made in parts so that several intermediate elements (bismuth, carbon, etc.) have been formed between. In either case there could be an aggregate devolution and "recovery" in alternation.

The complex equations mentioned above[1] are fascinating but inconclusive.

To assume that the average interspace, which, in a large number of careful determinations, averages about 47, should be called 52 because a symmetrical series of arithmetical progression which has no known connection with the matter foots up 52; to set 1.1 = 0.8 and again = 0.6 as the first term of two series of three terms each, where the third term, the position of the element between barium and radium, is assumed to be 34 when if radium is 36.9 it may well be 40, is to take much for granted even in a region so much infested by mathematics as this one is.

The equations are obtained by the further assumption that there is an alternate disintegration and reintegration of

[1] Devolution and Evolution of the Elements. Phil. Mag., [6] 15, 47.

the most permanent elements of the series: beryllium, calcium and barium losing from their theoretical values by increasing amounts after the manner of radium, while the intervening elements lose and then gain, but in the case of "protoradium" and radium there is strangely no loss.

The same equations cannot be applied to or derived from the other series, and the many remarkable relations adduced remain largely unexplained.

SECTION VIII—EVOLUTION AND DEVOLUTION.

The helix is a working model and it suggests that there is only one enduring stable assemblage of corpuscles between the "Urstoff" and hydrogen with its thousand corpuscles, and if that element be coronium, it has endured only under the exceptional conditions of the corona.

As the *vix generatrix* passed over each unit space in the first circle the conditions favored the formation of a new element. In this circle are the simplest forms of matter from hydrogen to helium. They appear abundantly in the nebulae; existing, and perhaps formed, near the absolute zero, where no heat vibrations could yet be predicted, and where unexplained electrical activities could cause the light of the nebulae. The helix prophesies the discovery of only one new element of low atomic weight, protofluorine.

On the completion of the first circle, a double momentum swelled the curve to a full octave culminating in the unique element carbon, the element of life, and in a second octave culminating in silicon, the basis of the rocks. In contrast to the corpuscular temperature or vibration within the atom in the elements of the nebulae, normal molecular vibration and normal electrical conditions become prevalent.

On passing potassium the treble momentum culminated in a double octave with the iron-nickel-cobalt group of the hot stars, the meteorites and the interior of the earth (see top of Fig. I). One may surmise that most of the heavy elements beyond this group are unimportant in the mass of the earth as they are in the meteorites. A considerable molecular radiation may have been a condition precedent to the addition

of a group of corpuscles equivalent to three hydrogen atoms, and the increasing complexity of the elements is indicated by their high and varying valence. Will three new elements be found to fill the gap below manganese, or will the outer triads be robbed for this purpose? The almost empty semicircle between ytterbium and tantalum is tantalizing, but the symmetry of the helix would rule out the gathering of the elements of the rare earths into a group like the triads, as has been suggested.

The sun carries the evolution a step further and it is conceivable that all the elements of the lowest-fusing quadrant have evaporated from it. Lead alone of the very heavy elements appears in the sun as a sort of "calx" or "caput mortuum," suggesting that evaporation into helium has reached its limit there. It is remarkable that at the farthest place from this quadrant, at the outermost curve of the high-fusing semicircle, the radium elements should be evaporating with explosive heat- and light-giving violence over all the surface of the earth, should exist in the outer layers of the earth only, and should be brought up by the light and highly acid pegmatite, whose quartz grains have been formed below 800°.[1] Becker's suggestion of the genesis of pegmatite with uranium as a potentializer of the energy that must escape in its formation is most interesting.[2]

When the assemblages had become so complex that devolution began to prevail over evolution, the size of the added group of corpuscles was increased to four, and a short advance only was made along the first quadruple-octave ring.

If ink is allowed to flow from a dropping tube, the point of which is immersed in water in a tall glass, the descending stream soon forms vortex rings and, as these rings sink and expand, they often become scalloped at the edges and the scallops expand in lobes which separate in distinct subordinate vortex rings while the central part closes in as an almost perfect ring again. Sometimes several of these lobes will separate symmetrically at the same time like the fluting on the border

[1] Day and Shepard: Am. J. Sci., **20**, 276 (1906).
[2] *Loc. cit.*, p. 143.

of a rose leaf. This is a model of the radium emanations and of the breaking up of the complex atoms. Thus is the limit set to the complexity of the atom and the length of the helix.

It has a mystical attractiveness that the helix has a shape like the spiral nebula from which all things have been thought to originate, and toward which they again tend, and that the tetrahedral element carbon stands in the center of this helix and by its shape (ranging from the tetrahedron, which includes the smallest amount of matter in unit surface, almost to the sphere, which contains the largest amount of matter in unit surface) typifies the infinite possibilities of life, of which it is the vehicle, and embodies the tetrahedral form which the earth has repeatedly, if imperfectly, approached.[1]

Furthermore the helix is a curious parallel of the solar system itself. They are both ring systems and, for the four small ring, there are the four small inner planets, and the two smallest rings match the two inner moonless planets.

For the four large rings there are the four large outer planets and as Jupiter, the first of them, is the culmination of the solar system, so the first large ring is the culmination of the elemental system, and furnishes in potassium, calcium, the iron group, etc., the major part of the basic elements for the meteorites, the earth, and perhaps for the whole planetary assemblage.

For the larger partial ring there stands the possibility of an outer planet.

OBITUARIES.

RUDOLPH FITTIG.

After a brief illness Rudolph Fittig died November 19, 1910. He was born at Hamburg, Germany, December 6, 1835, and was therefore nearly seventy-five years old at the time of his death. Fittig studied at Göttingen from 1856 to 1859. The moving spirit in the Göttingen laboratory at that time was, of course, Wöhler, whose chief interest was in inorganic chemistry. Limpricht had general charge of organic chemistry, and it was under him that Fittig did most of his work.

[1] T. Arldt: "Die Entwickelung der Erde" (1907), p. 506.

Among his contemporaries were Beilstein and Hübner. When Limpricht went to Greifswald, Beilstein had already gone to St. Petersburg, and this left the two young men, Fittig and Hübner, to take care of organic chemistry. Fittig became Privatdocent in 1860, and in 1866 he was made Professor *extraordinarius*. In 1870 he was called to Tübingen to take the place of Strecker, who had gone to Würzburg. He remained at Tübingen until 1876, when he accepted the professorship of chemistry in the University of Strassburg as the successor of Von Baeyer, who had been called to Munich. He performed the duties of the professorship in Strassburg until 1902, when he retired from active service, though he continued to live in Strassburg and occupied himself in rounding out his extensive investigations and preparing the results for publication. His work never stopped until his death, as far as the outside world can judge.

Fittig began his career as an investigator by some observations on acetone. He soon became interested in the aromatic compounds which were then coming into prominence. Nothing of much importance came of his work, however, until 1864, when his famous article, "The Synthesis of Methyl-phenyl by the Würtz Method", appeared in the *Annalen der Chemie*.[1] Tollens was associated with him in this piece of work and the article appeared under both names. Benzene had then been known for a number of years, but no helpful suggestion had up to that time been made regarding its relations to the paraffins. Toluene was also known and had received its place next to benzene in the aromatic series, but the relation between benzene and toluene was not at all clear to the chemists of that day. That the two differed from each other in composition as the successive members of an homologous series differ from each other was recognized, but the nature of homology was still a subject of discussion, and the question whether the then known toluene was a true homologue of benzene was unanswered. Würtz had devised a method of synthesis for the paraffins which has proved of great value in clearing up the relations between these hydrocarbons, and it occurred to Fittig to apply this method to the aromatic hydrocarbons. He first treated monobrombenzene with sodium and found that the bromine is easily removed, and that the two phenyl groups thus formed unite to form diphenyl:

$$2C_6H_5Br + 2Na = C_6H_5—C_6H_5 + 2NaBr.$$

The fact having been established that sodium has the power

[1] Vol. **131**, 303.

to remove the bromine from monobrombenzene, he next tried the action of sodium on a mixture of monobrombenzene and methyl bromide. The reaction took place as was expected, and a compound to which Fittig and Tollens gave the name methyl-phenyl was formed:

$$C_6H_5Br + CH_3Br + 2Na = C_6H_5—CH_3 + 2NaBr.$$

They showed that their synthetical product was identical with toluene, and in discussing the result they used these words: "Accordingly toluene is benzene in which the radical methyl has been substituted for an atom of hydrogen."

* * "Toluene is generally regarded as the second member of the benzene series, that is to say, as a true homologue of benzene. If this view is correct, the possibility is given of building up an homologous series from the initial member by means of such synthetical experiments, and, we may say, in general, that one substance is homologous to another, if in place of hydrogen in its radical it contains the radical methyl. Before, however, we can accept such a view in regard to the constitution of homologous compounds as correct, the question must first be answered, whether toluene really is a homologue of benzene, whether it bears to benzene the same relation, that, for example, ethyl compounds bear to methyl compounds. The conduct of the two hydrocarbons as far as it is at present known is well calculated to give a negative, rather than a positive, answer to the question."

This passage is very interesting historically, as it helps us to understand how our present clear-cut view of homology came to be accepted. Very shortly after the appearance of the article by Fittig and Tollens, Schorlemmer[1] showed that the compound made by extracting the chlorine from methyl chloride is identical with "ethyl hydride," that it is in fact ethane, the second member of the paraffin series. This result, taken together with that obtained by Fittig and Tollens, left no doubt in regard to the nature of homology, and since that time it has been glibly defined with little thought, generally speaking, as to how the explanation was reached. Fittig seems to have lost his doubts regarding the homology of toluene and benzene.

In 1866 Kekulé, in his famous article on aromatic compounds,[2] refers to Fittig's work thus: "The beautiful investigations of Fittig leave no room for doubt in regard to the constitution of these hydrocarbons." And much later,

[1] Ann. Chem. (Liebig), **132**, 234.

[2] *Ibid.*, **137**, 1141.

in 1890, when the German Chemical Society celebrated the 25th anniversary of the birth of his benzene theory, Kekulé again referred to Fittig's work. He tells of the way his theory of the constitution of chemical compounds came to him in a half-dreamy state and how he had put aside what he had written on this subject at that time. He then adds: "The same thing happened with the benzene theory. It lay nearly a year written out among my papers, until the beautiful synthesis of the aromatic hydrocarbons by Fittig and Tollens led me to publish what I had written."

The next important contribution of Fittig was one which showed mesitylene to be a trimethyl derivative of benzene. The two articles embodying the results of the investigation on mesitylene appeared in the *Annalen* in 1867 and 1868. He showed that by oxidation mesitylene yields successively a monobasic, a dibasic, and a tribasic acid, and that each stage involves the conversion of one methyl group into carboxyl. From the tribasic acid by distillation with lime benzene is formed, from the dibasic acid toluene is formed in the same way, and from the monobasic acid one of the xylenes. He says: "It follows, however, from the facts that mesitylene is a true trimethylbenzene, and that the following constitutional formulas must be assigned to the principal members of the mesitylene series:

$C_6H_3\{CH_3, CH_3, CH_3$	$C_6H_3\{CH_3, CH_3, COOH$	$C_6H_3\{CH_3, COOH, COOH$	$C_6H_3\{COOH, COOH, COOH$
Mesitylene.	**Mesitylenic acid.**	**Uvitic acid.**	**Trimesitic acid.**

Later it was shown that mesitylene is the symmetrical variety of trimethylbenzene and, that being established, it follows that the xylene obtained from mesitylenic acid must be the meta variety, and this becomes one of the fundamental facts upon which the classification of the di-substitution products of benzene into ortho, meta, and para rests.

It will be quite impossible to discuss all of Fittig's work as the two important contributions above referred to have been discussed. Indeed it is doubtful whether anything he did in the years after 1868 had as much influence on chemical thought as that which he did before this time.

It has already been stated that he was called to Tübingen in 1870. There he found conditions somewhat unfavorable. He had to do more lecturing and the laboratory was a sorry affair. Fittig had the most fastidious tastes so far as his laboratory surroundings were concerned. He was extremely

neat and orderly. In Tübingen things looked down at the heel and this seemed to worry him constantly. Nevertheless he went on with his work and accomplished much. During the six years of his life here he was rather feeling his way. Nothing very striking came of it. His work on phenanthrene led him to the view that the quinones are diketones and this view prevails at present. An investigation on sorbic acid and another on piperic acid interested him in unsaturated acids and these continued to occupy him several years. The results are embodied in a series of articles entitled "Untersuchungen über die ungesättigten Säuren," the first of which appeared in the *Annalen* in 1877 and the last in 1883.

His discovery of the lactones and the lactonic acids was announced in 1880 and a number of comprehensive articles on these compounds followed, extending to 1893.

His studies of the unsaturated acids led, among other things, to the interesting observation that some of these acids are subject to an internal change involving a "shifting of the double bond."

By invitation of the German Chemical Society, he gave a general account of his work on the unsaturated acids before the Society October 15, 1894. The address was published in the *Berichte*.[1] He tells in an interesting way how he came to take up this work and in general what object he had in view. The following characteristic passage may be quoted to advantage. He says: "My colleagues have repeatedly said to me that it is difficult to work through my bulky articles, and I believe many have asked whether it was necessary to collect such a mass of material and always to test the same reaction in so many special cases. Gentlemen, I can assure you that the preparation of new chemical compounds has never in my life had any attraction for me. When, however, I formed the plan for these investigations and spoke with my friends about it, I knew very well that the carrying out of the plan would require many years, for it was perfectly clear to me that no generalizations could be reached through the study of a few cases."

At the beginning of Fittig's work the field of the unsaturated acids was almost uncultivated. He has enriched it with almost innumerable discoveries and it has yielded an abundant harvest.

Fittig's work was characterized by great thoroughness and accuracy and he justly prided himself upon the fact that no one had ever convicted him of an experimental error! There

[1] Vol. **27**, 2658.

was, to be sure, a painful polemic between him and Wislicenus in regard to the bromine addition-product of angelic acid, but it turned out that the difference between the results obtained by the two observers was due to the fact that one worked on the south side of his laboratory, the other on the north side, and the light proved to be the determining factor in the reaction.

Fittig did not directly contribute to any extent to the theories of chemistry, though he furnished the material basis for profitable speculation, notably, as has been pointed out, in his earliest work on aromatic compounds. It is doubtful whether any text-book of chemistry has ever been written that had less reference to underlying theories than his "Grundriss der anorganischen Chemie" and his editions of "Wöhler's Grundriss der organischen Chemie." These books are made up of compact statements of facts and are extremely valuable for the purpose for which they were prepared. He was a clear lecturer and an excellent laboratory teacher. His insistence upon thoroughness was characteristic of everything he did, and those who had the privilege of working under him have every reason to be thankful for the influence exerted by him as a teacher. The writer of the sketch was closely associated with Fittig for four years, two years as a student at Göttingen and two years as assistant at Tübingen, and he always recalls these years with gratitude, conscious of the fact that this association played a large part in such intellectual regeneration as he has been permitted to experience.

IRA REMSEN.

FELIX B. AHRENS.

Felix B. Ahrens, Professor of Agricultural and Chemical Technology at the University of Breslau, founder and for fifteen years editor of the collection of chemical and chemical-technological monographs which bears his name, died November 14th after an illness of almost two years.

Ahrens was born in Danzig on October 23, 1863, and was therefore only 47 years old at the time of his death. He went to Berlin in 1882, intending to become a pharmacist, but a few years later he took up the study of chemistry in the university there and in 1886 received his Doctor's degree from the University of Breslau. He studied under Ladenburg for a time at Kiel, and was also an assistant under Ferdinand Cohn in the Institute of Plant Physiology at Breslau. From 1890 to 1894, he was first assistant in the Chemical Institute of the University of Breslau, when he was promoted to the chair which he occupied till his health compelled him to retire from active work in 1908. While with Ladenburg, he

carried out important investigations on the alkaloids. His later work was devoted chiefly to technical problems, and his contributions on coal tar, acetylene and the sulphite liquors are worthy of note. He had a peculiar gift for putting important scientific advances into popular language and also contributed largely to Ladenburg's Dictionary of Chemistry and other compilatory works. Under his guidance, his "Sammlung" has achieved a success which assures the continuance of this series of valuable monographs, each of which is written by an acknowledged authority in his field.

STANISLAUS VON KOSTANECKI.

On November 15th, Stanislaus von Kostanecki, widely known for his investigations on natural coloring substances, died from the effects of a painful operation he had undergone a few days before. He was only a little over 50 years old, having been born in Myszaków, Russian Poland, April 16, 1860. His first chemical training was received at the hands of Prof. Krug, at Posen, and in 1881 he went to Berlin where he came under the influence of Finkener and Liebermann. The latter made him his assistant in 1884 and together they published a number of important papers, that on "Oxyanthraquinone," especially, attracting wide attention. In 1886 he went to Mülhausen as Noetling's assistant, where he displayed such originality and activity that in 1890, when barely 30 years old, he was appointed "Ordinarius" at Berne and in three years had so built up his department that a new building had to be erected to accommodate the students flocking in ever-increasing numbers to his laboratory. Among his more important investigations may be mentioned the synthesis of gentisin and other natural coloring substances and the preparation of the mother substances, chromone, flavone and flavonole, and the exhaustive study of brasilin and curcumin. In 1903 he was awarded the Lavoisier medal by the French Chemical Society, and the Mülhausen Industrial Society gave him its gold medal. He was a member of the Krakau Academy of Sciences, a "Chevalier" of the Legion of Honor, an ex-officer of the German Chemical Society, and president of the Swiss Chemical Society. His activity continued unabated almost to the very day of his death and during the last summer he published three papers.

REVIEWS.

DIE GEWINNUNG DES BROMS IN DER KALIINDUSTRIE. Von DR. PHIL, MAX MITREITER, Betriebschemiker. Monographien über chemisch-technische Fabrikations-Methoden. Band XX. Mit 24 in den Text gedruckten Abbildungen. Halle a. S.: Wilhelm Knapp. 1910. pp. 54. Price, M. 2.

The technical production of bromine is confined to the United States and to Germany. When Frank, in 1865, began the technical production, the price was $23.00 per kilogram. It has fallen as low as 16 cents, and is now about forty cents.

The raw material utilized for the production of bromine in the potash works is the mother liquor resulting from the separation of potassium chloride from carnallite; it contains 0.2 to 0.3 per cent. magnesium bromide and the bromine is obtained by the chemical method or by electrolysis. In the chemical method the bromine is liberated by the action of chlorine on magnesium bromide. The work is carried on in the apparatus of Wünsche which involves the use of iron bromide, Fe_3Br_8, in refining the bromine, or by the newer method of Kubierschky; in this process a mixture of gaseous chlorine and bromine issues from the apparatus in which the carnallite mother-liquor is treated with chlorine and is conducted into a refining apparatus in which by simple distillation it is separated into its two components of different vapor tension. For the theory and description of this very ingenious, economical and interesting process, the monograph must be consulted.

The electrolysis of the magnesium bromide is difficult because the amount of this salt in the mother liquor is so small. The methods first adopted have been abandoned; only one method is now in practical use, though the author describes two others as promising; the whole subject seems to be as yet in the experimental stage.

The process in use is that of Kossuth. The apparatus consists of stone-ware vats about four feet long, two wide and one deep, in which thirty-three carbon slabs are so placed that every portion of the liquid in its passage through the vat must come in contact with the electrodes. The magnesium bromide and a small amount of magnesium chloride are electrolyzed; the chlorine resulting from the latter salt displaces bromine in the bromide. The bromine remains dissolved in the liquid and is separated by fractional distillation.

Much bromine is marketed as iron bromide, Fe_3Br_8, which is to bromine what bleaching powder is to chlorine—a con-

venient carrier; it is sold in this form to the chemical factories where it is employed for making potassium, sodium and ammonium bromides. The Stassfurt works prepare free bromine, iron bromide and "brom-salt." This substance is used in large quantities in the extraction of gold from its ores and consists of a mixture of one equivalent of sodium bromate and two of sodium bromide; by the action of bromine on concentrated sodium hydroxide the mixture $NaBrO_3 + 5NaBr$ results, and this is mixed with more sodium bromate (made in other factories by electrolysis of sodium bromide) to obtain the proportion $NaBrO_3 + 2NaBr$.

The monograph is one of the most interesting of this series and will repay study. E. R.

DIE CHEMIE DER CELLULOSE, unter besonderer Berücksichtigung der Textil- und Zellstoffindustrien. Von DR. PHIL. CARL G. SCHWALBE, a.o. Professor an der Grossh Techn. Hochschule zu Darmstadt. Erste Hälfte. Berlin: Verlag von Gebrüder Borntraeger. 1910. pp. 272. Price, M. 9.60.

To those interested in the chemistry of cellulose, Professor Schwalbe's book will be a welcome addition to the few really good books on the subject.

Since Cross and Bevan wrote their "Cellulose" and "Researches," a large amount of work has been done on cellulose, and to a considerable extent this work has been published in scattered fragments in journals widely different in character and many in number. The peculiar merit of Professor Schwalbe's book is the bringing together of this large number of separate bits of work and coördinating them in a systematic study of the field as now known.

When one notes that there are nearly eleven hundred references to original work in this first half of 272 pages, the force of the statement about the collecting of others' work becomes apparent.

He has of course gone back much further than the recent work in his search—indeed usually to the very beginning.

This material is systematically arranged, so that the book becomes of great value as a means of looking up original work.

The book is of course much more than a mere collection of the work of others. It represents the thought and judgment of Professor Schwalbe and his interpretation of the results of research, together with contributions of his own to the work. His personal opinion in disputed points is always quite evident, but opposing views are fairly stated on the whole.

The reviewer heartily recommends the book to all interested in the chemistry of cellulose, and looks forward to the appearance of the second half of the work with great interest.

GEORGE S. TILLEY.